SYNTHESIS AND CHARACTERIZATION OF TPA LOADED
MESOPOROUS CATALYSTS AND THEIR PERFORMANCE IN PYROLYSIS
OF POLYPROPYLENE

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SYNTHESIS AND CHARACTERIZATION OF TPA LOADED MESOPOROUS CATALYSTS AND THEIR PERFORMANCE IN PYROLYSIS OF POLYPROPYLENE

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ABSTRACT

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Plastic materials have attracted attention in recent years because of their functionalities therefore; they are widely used in household and industry. As their usage increases, plastic waste amount also increases and this is an important environmental problem. Chemical recycling of these materials is a useful method to solve this problem because plastic materials can be converted into petrochemical feedstock with this method.

In this study, tungstophosphoric acid (TPA) loaded SBA-15 materials were synthesized hydrothermally to be used in degradation of polypropylene. TPA was incorporated to the porous framework of SBA-15 with different W/Si ratios. The synthesized catalysts characterized using XRD, Nitrogen Physisorption technique, SEM and FTIR and their performances were tested in TGA.

XRD analysis revealed that introducing TPA did not cause deformations in the regularity and the catalysts showed an amorphous structure. N_2 adsorption-

desorption isotherms showed that the synthesized materials exhibited type IV isotherms. The surface areas of the samples were in the range of 478-786 m^2/g depending on the amount of TPA loaded. Pore size distributions showed their mesoporosity. The average pore sizes were approximately 7.0 nm. SEM images indicated the hexagonal structure. DRIFTS spectra showed that TPA loading resulted in the formation of Brønsted acid sites and as the amount of TPA increased, the peak intensity of the Brønsted acidity increased. TG analysis revealed that when catalyst amount used in the experiments and TPA amount loaded into the materials increased, the degradation temperature decreased. Activation energy values of the samples were between 92.5 and 165.8 kJ/mole depending on the TPA loading amount and they are lower than that of pure polypropylene degradation reaction.

Keywords: Catalytic degradation, polypropylene, mesoporous, SBA-15, tungstophosphoric acid

ÖZ

TPA YÜKLENMIŞ MEZOGÖZENEKLİ KATALİZÖRLERİN SENTEZLENMESİ VE KARAKTERİZASYONU VE BU KATALİZÖRLERİN POLİPROPİLEN PİROLİZİNDEKİ PERFORMANSLARI

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Plastik malzemeler son yıllarda işlevselliklerinden dolayı ilgi çekmektedirler ve bu yüzden evlerde ve sanayide yaygın olarak kullanılmaktadır. Kullanımları arttıkça plastik atık miktarı da artmaktadır ve bu önemli bir çevresel problemdir. Bu malzemelerin kimyasal geri dönüşümü bu problemi çözmek için kullanışlı bir yöntemdir çünkü plastik malzemeler bu yöntemle petrokimya ham maddelerine dönüştürülebilirler.

Bu çalışmada tungstofosforik asit (TPA) yüklü SBA-15 maddeleri polipropilenin parçalanmasında kullanılmak üzere hidrotermal olarak sentezlenmiştir. TPA, SBA-15'in gözenekli yapısına farklı W/Si oranlarında katılmıştır. Sentezlenen katalizörler XRD, Azot Adsorpsiyon/Desorpsiyon yöntemi, SEM ve FTIR kullanılarak karakterize edilmiş ve performansları termogravimetrik analiz cihazında test edilmiştir.

XRD analizleri TPA eklemenin malzemenin düzenliliğinde deformasyona sebep olmadığı ve sentezlenen katalizörlerin amorf yapı gösterdiğini ortaya çıkarmıştır. Azot adsorpsiyon/desorpsiyon izotermleri sentezlenen malzemelerin Tip IV izoterm sergilediğini göstermiştir. Yüklenen TPA miktarına bağlı olarak yüzey alanları 478-786 m^2/g aralığındadır. Gözenek boyut dağılımları mezogözenekli olduklarını göstermiştir. Ortalama gözenek boyutları 7.0 nm'dir. SEM görüntüleri hegzagonal yapılarını göstermiştir. DRIFT spektrumları, TPA yüklenmesinin Brønsted asit bölgelerinin oluşumunu sağladığını ve TPA miktarı arttıkça Brønsted asitlerinin tepe noktalarının şiddetinin arttığını göstermiştir. TG analizleri, deneylerde kullanılan katalizör miktarı ve malzemelere yüklenen TPA miktarı arttığında parçalanma sıcaklığının düştüğünü göstermiştir. Yüklenen TPA miktarına bağlı olarak malzemelerin eşik enerjisi değerleri 92.5 ile 165.8 kJ/mol arasındadır ve saf polipropilenin parçalanma reaksiyonundan düşüktür.

Anahtar sözcükler: Katalitik parçalanma, polipropilen, mezogözenekli, SBA-15, tungstofosforik asit

To my family,

ACKNOWLEDGEMENTS

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A: Pre exponential factor (s^{-1})

E: Activation energy of the reaction (J/mol)

M_i: Weight of component i (g)

MW_i: Molecular weight of component i (g/mol)

n_i: Number of moles of component i (mol)

n: Order of the reaction

R: Gas constant (8.314 J/K.mol)

T: Temperature (K)

t: Time (min)

Abbreviations

BET: Brunauer-Emmett-Teller

FTIR: Fourier Transform Infrared Spectroscopy

IUPAC: International Union of Pure and Applied Chemistry

TEOS: Tetraethyl orthosilicate

TGA: Thermal gravimetric analyzer

TPA: Tungstophosphoric acid

PE: Polyethylene

PET: Poly (ethylene terepthalate)

PP: Polypropylene

PS: Polystyrene

PVC: Poly (vinyl chloride)

SEM: Scanning Electron Microscopy

XRD: X-Ray diffractometer

CHAPTER 1

INTRODUCTION

In recent years, usage of the plastic materials was increased because of their low price, high production capacity and simple production techniques. Because of these qualifications, they were widely used in household appliances, packaging, automotive and aerospace components, construction, medicine and electronics. They are used to replace traditional materials such as metals, wood and glass. As well as the use of the plastics in daily life has been increased, plastic waste amount has been increasing. The disposal of these waste plastics is an important environmental problem. There are three main methods for the disposal of plastics. These are landfilling, incineration and recycling. Since plastics are not easily biodegradable, landfilling is not a suitable method for the disposal of these plastic wastes. Incineration is not an acceptable process because it pollutes air and environment by releasing toxic and greenhouse gases. Recycling can be divided into two as mechanical and chemical recycling. Mechanical recycling is a simple and cheap method but polymers can be converted only to the products of the same material. Therefore, an alternative method is chemical recycling which has attracted much interest recently with the aim of converting waste polymers into petrochemical feedstock.

Chemical recycling methods are gasification, hydrogenation and pyrolysis. Gasification is the partial oxidation of organic materials into syngas. This process is not profitable if the plant capacity is not very high. Hydrogenation is the addition of hydrogen by chemical reaction. This process also has disadvantages because of the cost of hydrogen and high pressure requirements. Pyrolysis is the

decomposition of polymeric materials by applying heat under inert atmospheric conditions. From the degradation of polymers, mainly olefins and aromatic organic compounds are produced and these products are then used as a source of many chemicals and fuels. Pyrolysis temperatures of polymers are high. Generally, a temperature value above $500^{o}C$ is needed for the decomposition in a typical pyrolysis reaction. Also, the distribution of the products has a wide range of carbon numbers, which is an unwanted situation because the desired products are in a specific range. Therefore, catalysts are used in most cases to decrease the energy consumption by decreasing the temperature and residence time of the reaction. They are also used to narrow the distribution of products and increase the product quality.

The most commonly used catalysts in plastic degradation reactions are solid acids: mainly alumina, amorphous silica-alumina, zeolites and some mesostructured materials. These are the catalysts generally used in the petroleum processing and petrochemical industries. Zeolites X, Y and ZSM-5, are the most commonly used zeolites for catalytic cracking reactions of polymers [1]. The acidity of zeolites are very high but they have micropores which obstruct the access of polymers into these pores. Therefore, mesostructured materials such as MCM-41 and SBA-15 are became important in the catalytic cracking of polymers. However, these materials also have a disadvantage due to their acidity. These materials have lower acidity than zeolites.

In order to make these mesostructured materials useful in catalytic cracking reactions, acid sites have to be introduced into these materials. For example, pure SBA-15 would have not showed significant catalytic activity if an appropriate acidic medium had been introduced into its structure [2]. For this purpose heteropolyacids were chosen to be introduced into mesoporous materials. Also, the acid sites in HPA are more uniform and easier to control than those in other solid acid catalysts. However, they cannot be used alone in these reactions because they have low thermal stability which leads to a restricted reaction temperature. There are many HPA types. Among these, Keggin structure HPAs

have the highest thermal stability. When acidity and thermal stability are compared, it is seen that TPA is the strongest acid with the best thermal stability among the other HPAs. Therefore, it is the best choice acid to be introduced to mesoporous materials.

In this study, TPA loaded SBA-15 materials were synthesized following a hydrothermal synthesis route. The synthesized catalysts were characterized using XRD, N_2 Adsorpsion/Desorpsion technique, SEM and FTIR and the performance of the synthesized materials were tested by thermogravimetric analysis.

CHAPTER 2

POLYMERS

The word polymer is derived from the Greek words 'poly' meaning many and 'meros' meaning part. A polymer is a large molecule made up of countless smaller molecules. It may be linear, branched, or interconnected. The small molecules used as the basic building blocks for these large molecules are known as monomers [3]. For example, ethylene is the monomer of polyethylene and propylene is the monomer of polypropylene. The size of a polymer molecule may be described either by its mass or by the number of repeat units in the molecule which is called the degree of polymerization [3]. Polymers can be either rigid or flexible and may be either brittle or very elastic. Unlike metals and ceramics, the physical properties of polymers can change significantly with temperature and pressure. For example, a change in the ambient temperature converts a brittle rigid plastic to a soft and extensible elastomer [4].

2.1 Historical Development

In 1811, Henry Braconnot, a French chemist, worked on derivative cellulose compounds and this study is probably the earliest study in the history of polymers. Then, in the 19th century, the durability of the natural polymer rubber which signifies the first popularized semi-synthetic polymer was improved by the development of vulcanization. In 1907, Bakelite, the first completely synthetic polymer, was created by Leo Baekeland, a Belgian chemist, by reacting formaldehyde and phenol at precisely controlled temperature and pressure. In

1922, Hermann Staudinger, a German chemist, came up with an idea which did not gain wide acceptance for over a decade and for which he was awarded the Nobel Prize that polymers consisted of long chains of atoms connected by covalent bonds. In 1920s, Wallace Carothers worked on synthesizing polymers from their monomer units. In 1963, Ziegler-Natta catalyst which is an important contribution to synthetic polymer science was developed by Giulio Natta, an Italian chemist, and Karl Ziegler, a German chemist. Another Nobel Prize was awarded in 1974 by Paul Flory whose extensive work on polymers included the kinetics of step-growth polymerization and of addition polymerization, chain transfer, excluded volume, the Flory-Huggins solution theory, and the Flory convention [5].

2.2 Classification of Polymers

Polymers are classified according to different properties such as their origin, structure, thermal behaviour, monomer composition, polymerization mechanism or chain configurations. When classified by origin, polymers divided into four groups as synthetic organic polymers, biopolymers, semi-synthetic polymers and inorganic polymers. When classified by structure, there are four chain structures as linear chains, branched chains, polymer networks and ladder polymers. Polymers divided into two groups as thermoplastics and thermosets according to their thermal behaviour. When classified by monomer composition, polymers are grouped such as homopolymers, random copolymers, alternating copolymers, block copolymers. Polymerization mechanism is another classification method and condensation and addition polymerization are examples of this group. When polymers classified by chain configuration, they are divided into three groups as monomer orientation, geometric isomerism and stereoisomerism [6]. Between these groups, thermal behaviour is the most important classification that has to be focused on.

2.2.1 Thermoplastic Polymers

Thermoplastic polymer is called to plastics which are soften increasingly until they are close to liquids when they are heated in the absence of oxygen. They are made up of long-chain molecules which are not chemically joined to each other. They can be formed into a shape many times. When heated, they will soften, when cooled they will set. They can change from rigid to extremely flexible, and in general the flexibility increases as the temperature increases, although sometimes this is not very apparent until their temperature rises up to a level at which they definitely begin to soften [7]. Some examples for thermoplastics are polypropylene, high density and low density polyethylene, PVC, PET and polyamide (Nylon 6).

Thermoplastic polymer can be created by chain growth or step growth reactions. In either case the polymer chains consist of a string of monomer residues, each of which is attached to two other monomer residues.

2.2.2 Thermosetting Polymers

A thermosetting polymer does not liquify when heat and pressure are applied. They do not dissolve in solvents, but they can soften and swell. They are composed of an interconnected network of chains which are chemically connected to their neighbours, either directly or through short bridging chains. These networks are called crosslinked [8].

Thermosets are nearly non-flexible and can only be formed into a shape once. Latter heating process performed to transform the shape will not have the desired effect. Examples for thermosets are bakalite, melamine, formica, ebonite, etc. [7].

There are two ways two create thermosettling polymers. Firstly, they are formed directly by step growth reactions. To form a thermoset by step growth, an

important proportion of tri- or higher functional monomers are required. Secondly, they can be form by crosslinking a thermoplastic polymer. Linear polymers can be crosslinked to create thermosets through various reactions, due to the different chemical structures of the starting polymers [8].

2.3 Well-known Polymers

In daily life, some thermoplastic polymers are generally used and very well-known by most of the people. Examples for these thermoplastics are polypropylene, polyethylene, polystyrene, polyvinyl chloride and polyethylene terephtalate.

2.3.1 Polyethylene

Polyethylene (PE) is a polymer consisting of long chains of the ethylene monomer. It is produced through polymerization of ethylene. In Figure 2.1 space-filling model of polyethylene is given.
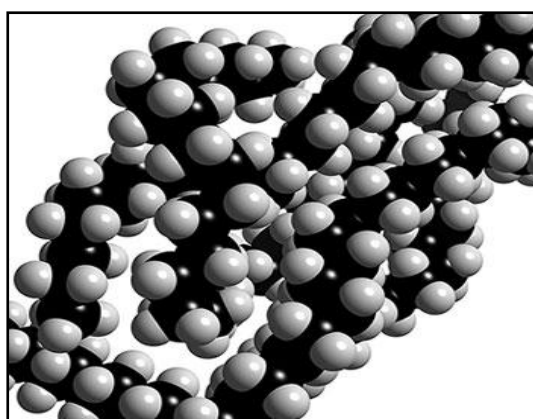
Figure 2.1 Space-filling model of polyethylene (black circles: carbon, grey circles: hydrogen) [9]

Polyethylene is a thermoplastic with a density less than the density of water. Its melting point is between 80 and 130°C. It is translucent or opaque but thin films may be transparent [10]. It is very flexible and this property provides easy processing which means it does not need to be dried before processing and this property makes PE a low-cost material for making lots of products such as squeeze bottles, films and sheets. PE has low moisture absorptivity which increases the easy processing. Low moisture absorptivity also improves the electrical insulation properties of PE because electrical conductivity loses its importance when moisture is absent. PE has good toughness and impact properties. Under tension, PE shows very high stretch and has high elongation values. PE has good chemical resistance to most acids, alkali and salts [11]. Polyethylene is classified into several different categories based mostly on its density and branching. Some of these PE types and their properties were given in Table 2.1.

Table 2.1 Properties of some types of polyethylene [11]

Properties	Low-density polyethylene (LDPE)	Medium-density polyethylene (MDPE)	Linear low-density polyethylene (LLDPE)	High-density polyethylene (HDPE)
Density (g/cm^3)	0.910-0.925	0.926-0.940	0.916-0.930	0.941-0.958
Melting Point (°C)	110	125	122-124	138
Melt Mass Flow Rate (g/10min)	0.12-10	0.04-6.4	0.20-4.1	0.020-9.0
Yield Tensile Strength (MPa)	9-14	21	9-19	26-33
Ultimate Tensile Strength	10-12	29	13-15	30-32
Flexural Modulus (MPa)	240-330	700	275-720	1000-1550

Polyethylene has many applications due to its low cost, easy processability, excellent electrical insulation and chemical resistance, toughness and flexibility, freedom from odour and toxicity [10]. Some examples to these applications are carrier bags, cases, industrial containers, garbage containers, food containers, buckets, industrial packaging, food packaging, housewares, toys, bottles for milk and other foodstuffs, household chemicals, drug packaging and detergents, domestic water and gas piping, agricultural piping, ink tubes for ball point pens, cable and other wire-covering applications [10, 11].

2.3.2 Polypropylene

Polypropylene (PP) is the second most common linear thermoplastic of the polyolefin family [12]. The macromolecule of PP contains 10000 to 20000 monomer units. In Figure 2.2, space filling model of polypropylene is given. It was first produced by G. Natta, following the work of K. Ziegler in 1954 [13]. It is a semi-crystalline thermoplastic mainly produced by stereospecific polymerization process to obtain highly regular chain structures. It is produced by low pressure polymerization using Ziegler-Natta catalysts [12].
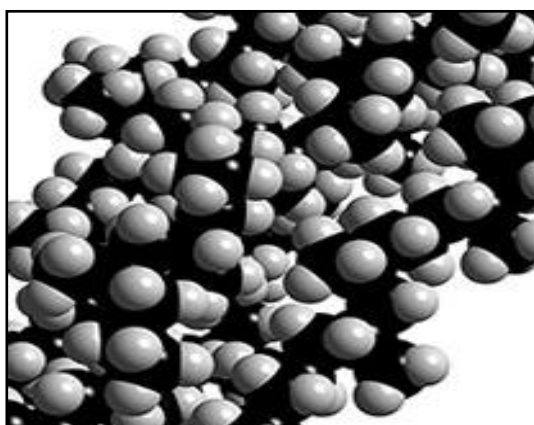
Figure 2.2 Space-filling model of polypropylene (black circles: carbon, grey circles: hydrogen) [14]

Stereospecific catalysts control the position of the side group. In PP, this side group is methyl group. The location of the methyl groups in the chain may change. If all the groups are on the same side of the polymer chain, the product is called as isotactic polypropylene. 90% of the produced polypropylene is isotactic when low pressure polymerization process is applied and Ziegler-Natta catalysts are used [12]. The other forms of PP are syndiotactic, atactic, etc. If methyl groups are attached to the chain in an alternating behavior, the product is called as syndiotactic polypropylene. And, if pendant groups are attached in a random behavior, the polypropylene is called atactic [13]. Some other production processes are used for production of PP such as solvent (slurry) polymerization and gas-phase polymerization [12].

Polypropylene shows good fatigue resistance, good environmental stress cracking resistance, good hardness [13]. It has excellent insulating properties. It is not soluble at room temperature, but dissolves in hydrocarbons and chlorinated hydrocarbons at temperatures above 80°C. It has excellent resistance to organic solvents, has good resistance to heat. The thermal degradation of PP begins at temperatures above 330°C [12]. Application area of polypropylene is very large and some of these were summarized in Table 2.2.

Table 2.2 Applications of Polypropylene [13]

Sector	Applications
Household goods	Buckets, bowls, bottle crates, toys, bottle caps, bottles, food processor housing, video cassettes, luggage
Automotive industry	Radiator expansion tanks, brake fluid reservoir fittings, steering wheel covers, wheel arch liner, bumpers, bumper covers, side strips, spoilers, mudguards, battery cases, tool boxes

Table 2.2 (con'd) Applications of Polypropylene [13]

Sector	Applications
Fibres	Artificial sport surfaces, monoflaments for rope and cordage, stretched tapes, woven carpet backing, packaging sacks and tarpaulins, staple fibres, filament yarns, fine fibres
Packaging	Margarine and ice-cream tubs, films, compartmentalised meal trays, thin-walled packaging for, e.g., disposable food trays, dessert cups and confectionery boxes, strapping tapes, blister packaging
Furniture	Stackable chairs
Domestic Appliances	Dishwasher parts such as top frame, basement, tubs, extruded gaskets, water duct, water softener compartment, etc. Washing machine parts such as detergent dispenser, door frames, inlet and outlet pipes, bellows, feet and wheel, housing and ducts, etc. Refrigerator parts such as boxes, containers, drawers, ducts, inlet and outlet pipes, etc. Microwave oven cabinet, irons and coffee maker body parts.
Pipes and Fittings	Solid rods, punching plates, hot wire reservoirs, tower packings for distillation columns, domestis wastewater pipes, pressure pipes, heat exchanger, corrugated pipes, smaller tubing, e.g., ballpoint cartridges, drinking straws

2.3.3 Polystyrene

Polystyrene (PS) is a color free, transparent thermoplastic polymer. It is amorphous or non-crystalline. It is a very clear material with good optical properties. Glass transition temperature (Tg) of polystyrene is 100°C and at room temperature PS is quite below this temperature, therefore it is brittle but hard.

Above Tg, PS softens easily, however, it does not show a definite melting point due to its amorphous structure. It has good resistance to water absorption; therefore, it does not need to be dried before processing. Raw materials for polystyrene production are styrene or vinyl benzene [11]. In Figure 2.3, space filling model of polystyrene is given.
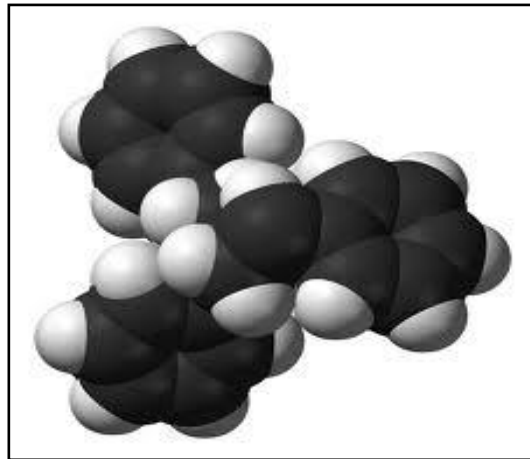
Figure 2.3 Space-filling model of polystyrene (black circles: carbon,
grey circles: hydrogen) [15]

Polystyrene does not have odour or taste. It has a specific gravity of 1.054. The chemical resistance of polystyrene is not generally as good as that of polyethylene. It is dissolved by a number of hydrocarbons such as benzene, toluene and ethylbenzene, by chlorinated hydrocarbons such as carbon tetrachloride, chloroform and o-dichlorobenzene, by a number of ketones (but not acetone), and esters and by a few oils. Many other materials, in particular acids, alcohols, oils, cosmetic creams and foodstuffs, will cause crazing and cracking and in some cases chemical decomposition. It is not toxic. It has good electrical insulation properties, low water absorption and comparatively easy processability [10].

Packaging is the largest application area for PS and includes such products as food and dairy containers, closures, lids, produce trays and baskets, vending cups and fast food containers. Electronics such as video cassettes, reels, audio/video, CD and DVD cases or jewel boxes; wash machine control panel, television panel, smoke detector housings; tumblers, plates, toys, cutlery, air conditioner and fan grills, refrigerator parts, syringes, culture dishes and test tubes, egg cartons, etc. Also, PS foams are good thermal insulators and used as building insulation materials [11].

2.3.4 Poly(vinyl chloride)

Poly(vinyl chloride) (PVC) is a thermoplastic polymer which is produced by polymerization of the vinyl chloride monomer. It consists of vinyl groups that are repeatedly present in the backbone. In Figure 2.4, space filling model of poly(vinyl chloride) is given.
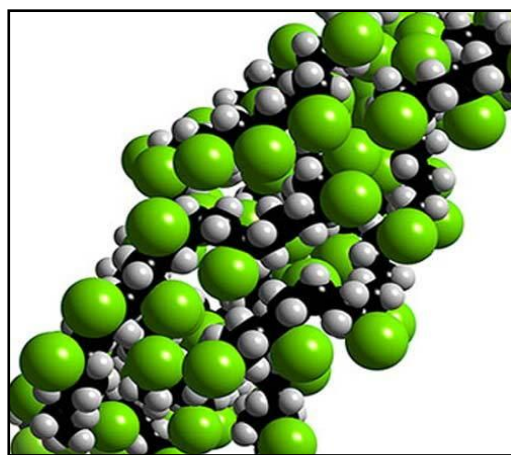
Figure 2.4 Space-filling model of poly(vinyl chloride) (black circles: carbon, grey circles: hydrogen, green circles: chloride) [16]

PVC is hard, quite brittle polymer. Plasticization can change the basic plastics to give a soft and flexible material. Chemically, it is resistant to acids, alkalis and many solvents; however, it dissolves in ketones, esters and, to certain extent, chlorinated hydrocarbons. Due to the presence of chlorine atoms in the molecule it is significantly more flame resistant than PE. PVC is an excellent electrical insulator and plasticized PVC is widely used for covering electrical wiring. It is also used for electrical conduits [7].

PVC is used in windows and doors, garden hoses, film and sheets for food wrap, crash pads, refrigerator gaskets, insulation for electrical wires and communication cables, pipes and fittings, automotive parts, pool linings and flooring, shower curtains, tablecloths, rain wear, dish washer racks, etc. [11].

2.3.5 Poly(ethylene terephtalate)

Poly(ethylene terepthalate) (PET) is a thermoplastic polymer resin of the polyester family with the repeating unit of $C_{10}H_8O_4$. In Figure 2.5, space filling model of poly(ethylene terepthalate) is given.
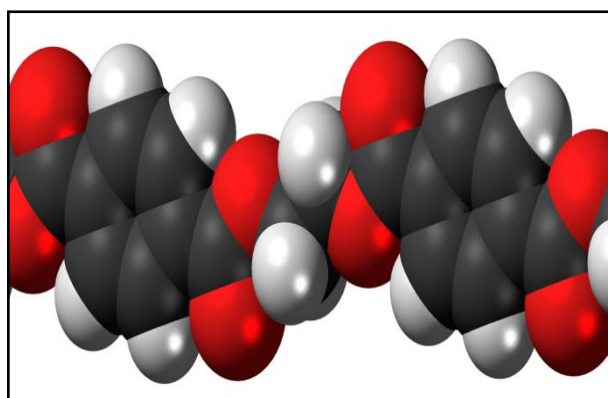
Figure 2.5 Space-filling model of poly(ethylene terepthalate) (black circles: carbon, grey circles: hydrogen, red circles: oxygen) [17]

PET has high crystallinity and clarity. It has low moisture absorptivity but it needs to be dried before processing. It has good chemical resistance to weak mineral acids and alkali but dissolves in concentrated sulfuric acid and nitric acid. It has very good electrical insulation properties at room temperature. It is transparent, tough and stiff [11].

PET is mostly used in pop-bottle and fiber-type applications. Pop-bottles are the best-known to be soft drink bottles. PET fiber is used in clothing in place of wool and cotton or in pillows as fillers. Examples of other applications are food packaging, pharmaceutical and cosmetic packaging, photographic and x-ray films, solar panel films, audio and video tapes, etc. [11].

2.4 Disposal Methods

Plastic materials are disposed generally with three main methods which are landfilling, incineration and recycling. Recycling is done by two methods, mechanical and chemical recycling. One of these methods, chemical recycling is a promising method with many advantages.

2.4.1 Landfilling

Historically, landfills have been the most common methods of organized waste disposal and remain so in many places around the world. During waste decomposition in a landfill, oxygen is present in the void space. It gives rise to aerobic decomposition. At that time, biodegradable organic materials react quickly with oxygen to form carbon dioxide, water, and other by-products [18]. Landfills contain significant contaminants that can pollute soil and water. Also, they contain large amounts of carbon dioxide, methane, and other toxic gases that resulted in the greenhouse effect [19]. However, plastics should not be put in a landfill for disposal because most synthetic plastics do not decompose

dramatically with time and therefore the landfills cannot be reused in the near future. Because of these reasons, landfilling is not a good method for the plastic disposal.

2.4.2 Incineration

Incineration is the most common thermal treatment process for organic contaminants in industrial and municipal wastes. Incineration simply is heating wastes in the presence of oxygen to oxidize organic compounds [20].

This basic method, in one or more of its very large number of modifications, appears to be one of the most universally satisfactory methods for disposal of many forms of solid wastes, including plastics. However, volume reduction for all wastes ranges from 70-80%, with a weight reduction to between 60% and 80% achievable depending on original charge. Plastics, if burned alone, would be almost completely incinerated, giving a weight reduction of well over 95% but still not 100%. Also, it is a source of annoying air pollution because of poor combustion or because some of the gaseous, liquid or solid combustion products are carried of in the exhaust gases [21]. Therefore, incineration is not a suitable process because in this process all of the waste cannot be decomposed and also it pollutes air and environment by releasing toxic and greenhouse gases.

2.4.3 Recycling

Recycling allows the wastes to enter the consumption cycle again, usually in secondary applications. Plastics can be recycled using two different methods: mechanical and chemical recycling. In the first, the plastics are recycled as polymers, while in the second, plastic wastes are turned into chemicals or fuels [22].

2.4.3.1 Mechanical Recycling

Mechanical recycling (i.e. secondary or material recycling) is the process with an aim of regaining the material but not destroying the chemical structure of the waste material and not energy saving or disposal [23].

In mechanical recycling, the waste must get through a sorting and cleaning operations because of three reasons. Firstly, mixed plastic fractions decrease the product quality. Secondly, plastics have different melting and processing temperatures. Lastly, food residues from various containers or paper labels or glue residues or some other materials which were used in combination with plastics can be found as contaminants of plastics. Therefore, an ordinary mechanical recycling path for waste plastics can be divided into two types of processes; mechanical treatment and melt processing. Mechanical treatment includes storage, size reduction, washing and sorting the waste. Melt processing would include regranulation and reprocessing. Size reduction is needed because the material particles must have an appropriate size for further applications. Washing is needed to clear off any dirt and residues stick to waste plastic [24]. Identification and sorting is needed because mechanical recycling of plastic waste can only be applied on single polymer plastic [20]. After mechanical treatment, plastics are ready to process and these processes are extrusion, injection moulding, blow moulding, compression moulding, etc. [24]. Comparison of these processes was given in Table 2.3.

Table 2.3 Comparison of melt processing methods [24]

Process	Complexity of parts	Forming action	Plastic types	Tolerance to contaminants
Extrusion	Fairly simple profiles	Extrusion	Single	Low
Injection moulding	Complex	Injection	Single	Low
Co-injection moulding	Complex	Injection	Single layers	Low
Compression moulding	Simple	Compression	Single	Medium
Extrusion blow moulding	Complex	Inflation	Single	Very low
Multi-layer extrusion blow moulding	Complex	Inflation	Single layers	Very low
Injection blow moulding	Simple	Inflation	Single	Very low
Film blowing	Simple	Inflation	Single	Very low
Intrusion moulding	Simple	Compression	Mixed	High
Sinter moulding	Simple	Compression	Mixed	Very High
Transfer moulding	Simple	Compression	Mixed	High

Examples of products found in our daily lives that come from mechanical recycling processes are grocery bags, pipes, gutters, window and door profiles, shutters, blinds and so on. This method is usable when the waste is composed of only one type of plastic. When the waste contains two or more types of plastics, applying this method is very hard.

2.4.3.2 Chemical Recycling

Chemical recycling, also known as feedstock recycling or tertiary recycling, aims to convert waste polymer into original monomers or other valuable chemicals. These products are useful as feedstock for a variety of downstream industrial processes or as transportation fuels [25].

This method is named as chemical recycling because in this method there is an alteration which takes place in the chemical structure of the polymer. In this process, waste plastics are not needed to be sorted and cleaned before processing because this process can be applied on heterogeneous and contaminated plastics. When recycled chemically, plastics give valuable products such as fuels and synthetic lubricants [20].

Chemical recycling is done by high temperature applications. Thermochemical treatments of plastics ended up with high product capacity but minimum waste. They enable the monomer yield up to 60% and produce valuable petrochemicals containing gases which consist mainly of refinery products and hydrocarbons, tars and char. Thermolysis processes can be split into three as gasification, hydrogenation (or hydrocracking) and pyrolysis (thermal cracking in an inert atmosphere) [20].

2.4.3.2.1 Gasification

Gasification can be defined as the partial oxidation of organic materials into gaseous product called 'synthesis gas' or 'syngas' which consists mainly of H_2, CO and small amounts of methane (CH_4), water vapour, CO_2, N_2 and the tar [19]. It was initially improved for coal conversion; however, it has been later used in the production of heavy petroleum gases and natural gas. In the last years, it has also been studied as a method of producing valuable chemicals from both biomass-derived products and organic solid residues [22].

Gasification may occur over a wide range of temperatures (700-1600°C) and pressures (10-90 atm) [22]. Air, poor oxygen, steam or a mixture of these gases can be used as the oxidant for the gasification process. Air-based gasification agents generally produce a gas which mainly consists of nitrogen with low heating value. Oxygen and steam-based gasification agents produce a gas which mainly consists of hydrogen and carbon monoxide with a higher heating value [20]. If the gasification agent is oxygen or air, its amount should be kept low in the reaction medium in order to prevent complete oxidation into CO_2 and water. The gasification process can be supported by metal catalysts, generally added to the raw material in aqueous solutions [22].

As the other thermochemical treatments, gasification has an advantage that plastics do not need to be separated before processing. However, the economics of this process mainly depend on the syngas. The important factors are the value and possible applications of this gas whether it is used as an energy source or used in the synthesis of various chemicals (methanol, ammonia, hydrocarbons, oxygenated compounds, *etc.*). Gasification can be seen as a feedstock recycling process for plastic wastes but the synthesis gas used in the synthesis of other chemicals mentioned above and not used as a fuel gas. Also, in order to make a profit from gasification, plants with capacities of about 400000-500000 tonnes/year should be in operation [22].

2.4.3.2.2 Hydrogenation

Hydrogenation is the addition of hydrogen by chemical reaction through unit operation [20]. Hydrogenation of plastic and rubber wastes is an alternative method for degrading the polymer chains. When compared to treatments without hydrogen usage, hydrogenation resulted in the production of highly saturated products, avoiding the presence of olefins in the liquid fractions, which favours their use as fuels without further treatment. Most of them need a catalyst to support hydrogen addition reactions. For this purpose, bifunctional catalysts are mainly used, combining both cracking and hydrogenation/dehydrogenation reactions. Generally, a catalyst includes transition metals (Pt, Ni, Mo, Fe, etc.) supported on solid acids like alumina, amorphous silica-alumina, zeolites, sulfated zirconia, etc. Also, hydrogen supports the elimination of heteroatoms (Cl, N and S) which may be present in the polymeric wastes. However, hydrogenation has many disadvantages. These are mainly the cost of hydrogen and the need for high pressure operation [22].

2.4.3.2.3 Pyrolysis

Pyrolysis is the thermal conversion of organic matter in the absence of oxygen at relatively low temperature values of 500 and 800°C and short vapour residence times of 3 to 1500 s. In pyrolysis, a liquid fuel is produced with solid char and some combustible gas. This fuel is generally used within the process to supply heat requirements or utilized of site in other thermal processes. The liquid fuel can be used instead of fuel oil in heat and power applications or to form a wide range of chemicals [20].

Pyrolysis is divided into two as non-catalytic (thermal) and catalytic pyrolysis. At high temperatures, thermal pyrolysis is possible but it is very energy consuming. In order to decrease energy consumption and narrow product distribution, catalysts are used in these processes and this process is called catalytic pyrolysis.

2.4.3.2.3.1 Non-catalytic Pyrolysis

In the non-catalytic (thermal) pyrolysis decomposition temperature is very high. Therefore a high amount of energy and time is necessary in order to achieve an efficient decomposition process. Also, the quality of the obtained products is low and the distribution of the products forms a broad range in terms of molecular weight or carbon atom numbers, which is actually not a preferred situation.

The product type and distribution obtained from the thermal pyrolysis of each polymer depends on some variables: the polymer itself, the reaction conditions, the type and working method of the reactor, *etc.* Among these variables, it is clear that the most important factor is the temperature, due to its effects both on the polymer conversion and the product distribution. From thermal pyrolysis of plastics and rubber materials, generally four types of products can be obtained depending on the classification due to physical states at room temperatures. These are gases, oils, solid waxes and a solid residue. When the temperature is increased, the gas yield increases and the solid residue turn into solid char because of the increase in the hydrocarbon coking reactions. Therefore, a wide range of products and applications can be obtained from the thermal degradation of polymers: fuel gases, olefinic gases, naphtha and middle distillates, oil fractions, long-chain paraffins and olefins, coke, *etc.* These products can be directly used as fuels or a source of chemicals. Besides, they can be further processed and improved in refineries to supply higher quality fuels [22].

Plastics and rubber thermally degraded through a radical mechanism. This may require three different decomposition pathways. The first one is random scission which occurs at any point in the polymer backbone. It causes the formation of smaller polymeric products. These products may further be subjected to additional random cracking reactions. The second one is end-chain scission. A small molecule and a long-chain polymeric material are formed in this pathway. If this small molecule is the starting monomer, the thermal decomposition process can be thought as a real depolymerization or unzipping process. The third one is the

extraction of functional substituents to produce small molecules. In this case, the polymer chain may keep its length or the release of the small molecule may occur with the division of the polymeric chain. In many situations several of these pathways occur at the same time. So that, polyethylene and polypropylene are degraded thermally by both random and end chain scissions. During the thermal decomposition of many polymers, some other reactions may occur simultaneously with the cracking reactions. These are isomerization, cyclization, aromatization, recombination of species, *etc.* [22].

2.4.3.2.3.2 Catalytic Pyrolysis

The catalytic pyrolysis of polymers has many advantages compared to the non-catalytic thermal pyrolysis. In the catalytic pyrolysis processes, decomposition temperature is efficiently reduced when compared to the non-catalytic thermal processes. This provides an efficient use of energy, which is a major concern. Also, the rate of reaction is higher in catalytic degradation, providing time efficiency as well. The quality and distribution of products is also enhanced in the presence of catalysts, making catalytic degradation a promising way to recycle waste polymers.

Different catalysts have been effectively used in the degradation of plastic materials. The most commonly used catalysts in plastic degradation reactions are solid acids: mainly alumina, amorphous silica-alumina and zeolites. These are the catalysts generally used in the petroleum processing and petrochemical industries. They have very different structural and acidic characteristics, which directly specify their catalytic activity and product selectivity. For example, alumina has Lewis acidity but amorphous silica-alumina and zeolites have both Brønsted and Lewis acid sites. This is a significant factor because the type of the acid site determines the initiation step of polymer degradation reactions. When Brønsted sites are present, proton addition occurs over these sites. However, when Lewis sites are present, hydride abstraction occurs. Therefore, the change in the initiation

step resulted in a change in the further steps and cracking reactions follow different pathways. In order to adjust the acidic concentration in amorphous silica-alumina and zeolites, Si/Al ratio can be changed because the concentration of these acids depends on this ratio which is due to the formation of acid sites by Al species. Also, the Al amount of the catalyst generally affects the strength of the acid sites. Stronger sites support the cracking reactions, however, they may also support undesired reactions like coke deposition and this may cause catalyst deactivation [22].

Activated carbon impregnated with transition metals and sulfated zirconia have also been tried in the catalytic cracking of polymers. Activated carbons are microporous solids with a graphitic-like structure and large surface areas. The incorporation of transition metals on activated carbon causes the formation of hydrogenating/dehydrogenating active sites. These active sites support hydrogen transfer reactions during plastic cracking reactions. Sulfated zirconia is known as a superacid solid. Its acidity is stronger than the acidity of 100% H_2SO_4 and therefore mainly used as a catalyst in reactions which needs strong acid sites [22].

Other attractive solids used in catalytic cracking of polymeric wastes are the silica-based mesophases. The most common member of this family is MCM-41. It has a hexagonal array of uniform pores with diameters which can be adjusted in the range of 1.5-10 nm by changing the synthesis conditions. These mesoporous materials can be formed with a wide range of framework compositions and show characteristics of zeolites and amorphous silica-alumina. These properties are uniformity of pore sizes, regular pore ordering, amorphous nature of the pore walls, presence of both Lewis and Brønsted acid sites of weak and medium strength, *etc.* Also, these materials have high surface areas, generally higher than 1000 m^2g^{-1}. Both the high surface area and uniform mesopores of MCM-41 promote the catalytic properties and this material has shown for the degradation of polyolefins [22].

CHAPTER 3

POROUS MATERIALS

There are three types of porous materials. According to the IUPAC definition, these are microporous (<2nm), mesoporous (2-50 nm) and macroporous (>50 nm) [26]. Porous materials are widely used as adsorbents, catalyst or catalyst supports and ion exchangers in many chemical and industrial applications [27, 28]. In heterogeneous catalysis, microporous and mesoporous materials are mainly used [29].

3.1 Microporous Materials

The best known members between the microporous materials are zeolites which have a narrow and uniform micropore size distribution. Particularly, zeolites have strongly taken interest as acids, but also as base and redox catalysts [30].

Zeolites are microporous crystalline silicoaluminates. They have a perfectly defined crystalline structure depending on the connection between SiO_4 and AlO_4 tetrahedra with oxygen bridges. Zeolites have pore sizes with a size below 1.0 nm. There are over 100 known zeolite structure types. Some of these zeolites are formed naturally; however, synthetic ones have the most important catalytic applications. Zeolites are classified according to their pore size (small, medium and large pore zeolites), the number of channel systems (unidimensional, bidimensional and tridimensional pore zeolites), and A1 content (low, medium and high silica alumina ratio zeolites) [22].

The A1 content can be changed by synthesis or post-synthesis methods. It is generally resulted in important changes in the acid strength of zeolites. Based on their structure and the Si/A1 ratio, both Brønsted and Lewis acid sites can exist in zeolites [22].

The characteristics of the zeolite channels are also important when their catalytic properties are explained. When zeolites are compared with amorphous silica-alumina, it can be seen that zeolitic catalysts have a number of advantages: a higher acid strength due to their crystalline structure, narrower pore size distribution, higher stability under thermal and hydrothermal conditions, lower rate of coke deposition, *etc.* The most common zeolites are: X, *Y,* ZSM-5, mordenite, *etc.* Also, these are the ones which are widely used in the catalytic cracking reactions of polymers. Figure 3.1 shows the structure of zeolites Y and ZSM-5 [22].
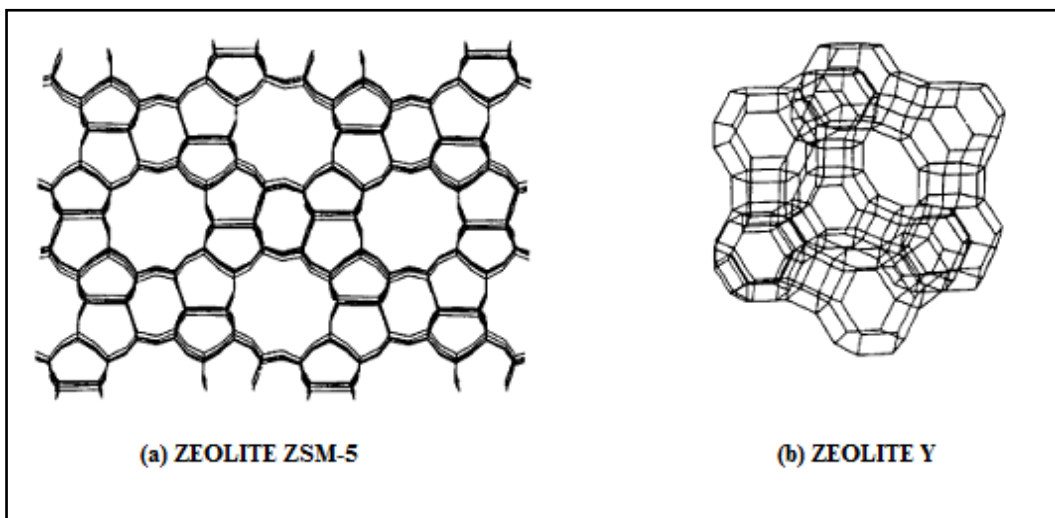

Figure 3.1 Pore structure of different zeolites: (a) ZSM-5, (b) Y [22]

The most significant disadvantage of zeolites is their pore size because when large molecules are present in the reaction, zeolites are limited because mass transfer limitations are frequently seen in microporous solids [29]. As a result, for the catalytic cracking of polymeric wastes, zeolites may not be preferable because of the structural and diffusional problems that polymer molecules may have when they are entering into the micropores of zeolites [22].

In addition to zeolites, pillared clays, some metal phosphates like titanium, zirconium etc., amorphous silica, inorganic gels and carbon molecular sieves are the members of microporous materials family [27, 31].

3.2 Mesoporous Materials

The improvement of oil production towards the processing of heavier crudes has built a demand for zeolites with larger pores, able to catalyze the conversion of very large hydrocarbon molecules. To overcome this demand, the researchers of Mobil worked on a new class of molecular sieves [32]. If the available molecular templates were too small to meet the required pore size, silica tetrahedral can be organized around larger objects. The incorporation of silicates to micellar systems has led the formation of mixed organic-inorganic mesophases corresponding to liquid crystal structures, with silica walls separating surfactant micelles. The removal of micelles allows formation of mesopores with a highly narrow pore size distribution. Their main accomplishments of mesoporous materials are the accessibility to large molecules, the ease with which their surface can be changed by transferred large active groups [32]. In order to produce a material with different pore sizes, surfactant can be changed [33]. However, the pores of these materials are irregularly arranged. The best known examples for mesoporous materials are M41S family (MCM-41, MCM-48, MCM-50) and SBA-15.

3.2.1 M41S Family and MCM-41

Mobile Research and Development Corporation synthesized a new family of ordered mesoporous silicates in 1992. This new family is called M41S. These new types of mesoporous structures have large surface areas and very narrow pore size distributions. The pore diameters can be varying from 1.5 to 10 nm. Changing the synthesis conditions different materials can be obtained. The research group defined three main phases: MCM-41 which is a hexagonal structure, MCM-48 which is a cubic structure and MCM-50 which is a lamellar structure [30, 34, 35]. These structures are shown in Figure 3.2.
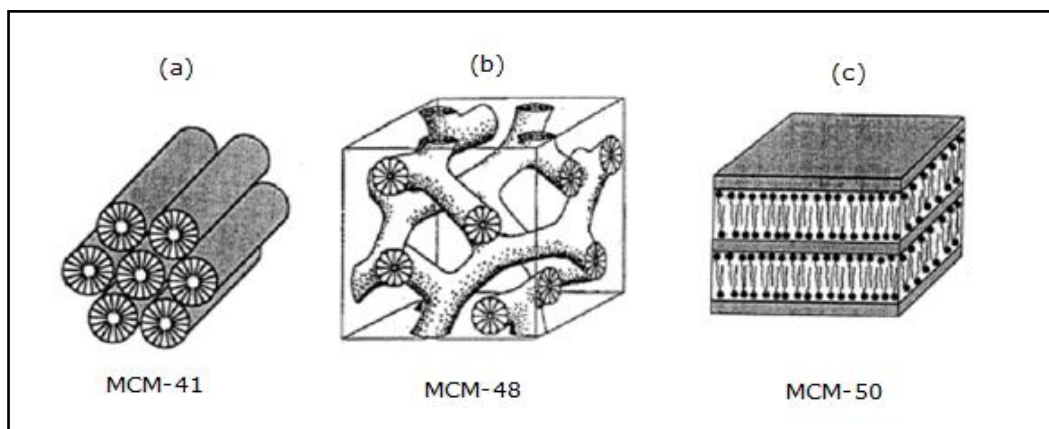
Figure 3.2 Three silica structures defined by Mobil researchers:
(a) MCM-41, (b) MCM-48, and (c) MCM-50 [36]

These mesoporous materials are produced by a 'liquid-crystal templating' (LCT) mechanism. In this mechanism (Figure 3.3), surfactant liquid crystal structures function as organic templates and inorganic material forms inorganic walls around the surfactant cylinders. After an ordered arrangement is achieved, thermal

process is applied to remove the organic material and produce a stable material [29, 37].
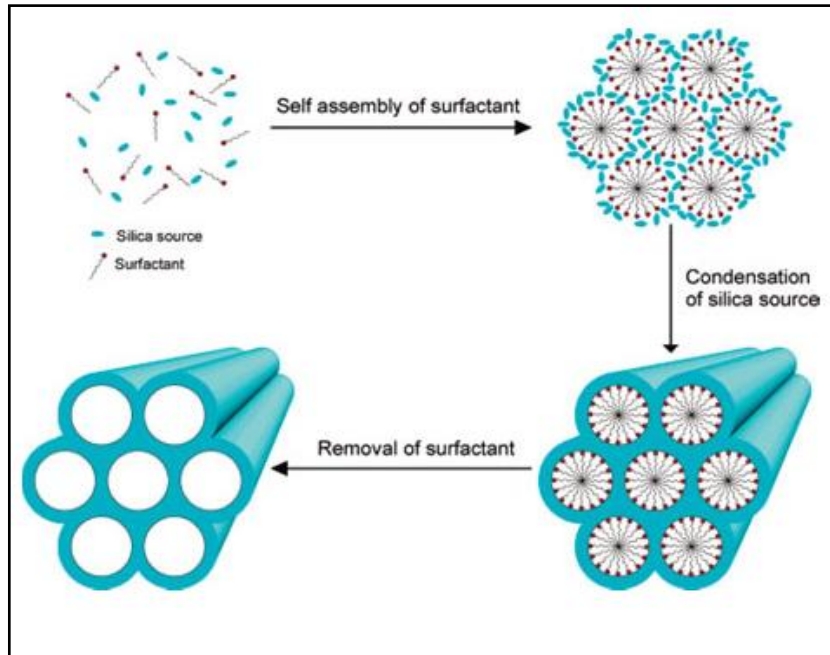
Figure 3.3 Formation mechanism of MCM-41 [38]

3.2.2 SBA-15

SBA-15, or Santa Barbara Amorphous type material, is a highly ordered, two dimensional and hexagonal mesostructured material [39]. A triblock copolymer, poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), is used in order to synthesize SBA-15. This material functions as templating agent in a highly acidic media [40]. SBA-15 has micropores in the form of interconnecting channels which binds hexagonal mesopores together (Figure 3.4) which is a

significant characteristic feature of SBA-15 [41]. This characteristic brings preferable and influential diffusion properties for the catalysis purposes.
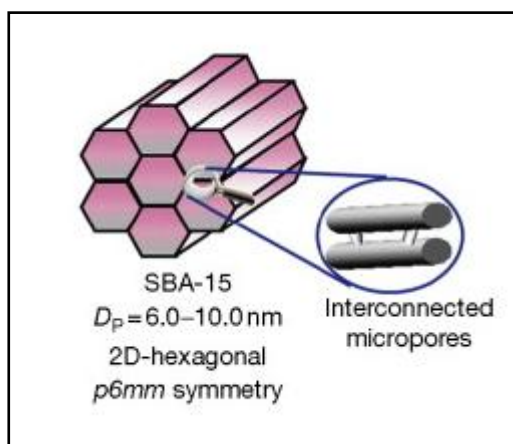
Figure 3.4 Schematical representation of SBA-15 [42]

SBA-15 is synthesized at an aging temperature range of 35°C to 80°C. Below and above this temperature range, SBA-15 could not be synthesized. Amorphous silica powder or poorly ordered products were obtained at room temperature. Above 80°C, only silica gel is produced. Hydrothermal synthesis temperature (35°-140°C) and time (11-72 hours) of SBA-15 in the reaction solution result in different pore size and wall thickness. The final product depends on the silica source. Tetraethoxysilane (TEOS), tetramethoxysilane (TMOS), and tetrapropoxysilane (TPOS) could be used for SBA-15 synthesis. The pH of the synthesis solution is another important variable to be set. In order to get an appropriate pH value which is lower than 1 to maintain an acidic medium, HCl, HBr, HI, HNO_3, H_2SO_4, or H_3PO_3 acids could be used. In the range of 2-6 pH values, precipitation or formation of silica gel could not be occurred. At pH 7, amorphous silica could be obtained [39].

SBA-15 represents a thick wall of 3–7 nm thickness and large pore sizes adjustable between 6 and 15 nm. When compared to mesoporous MCM-41 and related silicas, the thermal and hydrothermal stability are developed importantly by the thick wall of this material. The pore diameter of SBA-15 depends on the synthesis conditions. Increasing the gel aging temperature provides a larger pore diameter. SBA-15 has an interesting characteristic. It is the microporosity that is found in its mesopore wall, by which the micropores connect neighboring mesopores [30].

3.2.3 Modification of Mesoporous Materials with Heteropoly Acids

Heteropoly acids are type of acids composed of hydrogen and oxygen with particular metals and non-metals. Metals in the heteropoly acids are defined as the addenda atom like tungsten, vanadium or molybdenum. Non-metals are defined as the hetero atom and selected from the p-block of the periodic table, commonly silicon (Si) or phosphorus (P). In order to form heteropoly compounds, there must be at least two types of oxoanions. An example for the formation mechanism is given below:

$$12WO_4^{2-} + HPO_4^{2-} + 23H^+ -----> PW_{12}O_{40}^{3-} + 12H_2O \ \ [43]$$
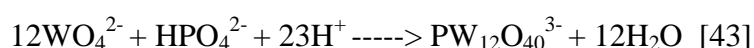
Silicon and phosphorus are the central atoms of the heteropoly anions. There are oxygen atoms binded to the central atom and metal atoms are around them. The structures of these compounds are commonly Keggin structure (Figure 3.5). Keggin structure has the general formula of $H_nXM_{12}O_{40}$ and Dawson structure has the general formula of $H_nX_2M_{18}O_{62}$ where X is the hetero atom and M is the addenda atom.
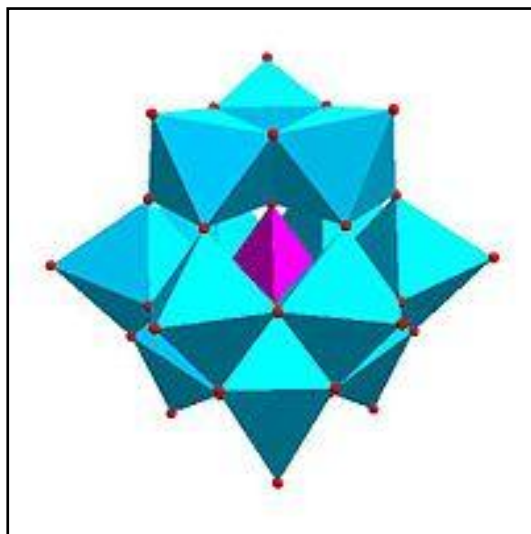
Figure 3.5 Keggin structure [44]

There are a lot of heteropoly acids because of the varying addenda atoms and hetero atoms. Well-known heteropoly acids are tunstophosphoric acid (TPA), silicotungstic acid (STA), silicomolybdic acid (SMA) and phosphomolybdic acid (PMA).

Tungstophosphoric acid (TPA), is a compound with colorless-grayish or yellow-green crystals. It is scentless and soluble in water. Generally, it exists as a hydrate. Its molecular formula is $H_3PW_{12}O_{40}$ where phosphorus is the hetero atom and tungsten is the addenda atom (Figure 3.6). It is not toxic but it is slightly irritating. This compound has many names such as phosphotungstic acid (PTA, PWA), 12-phosphotungstic acid, 12-tungstophosphoric acid and dodecatungstophosphoric acid [45]. The structure of TPA is Keggin structure where the anion has completely tetrahedral symmetry and includes a lattice of twelve tungsten atoms binded to the oxygen atoms with the phosphorus atom at its centre.
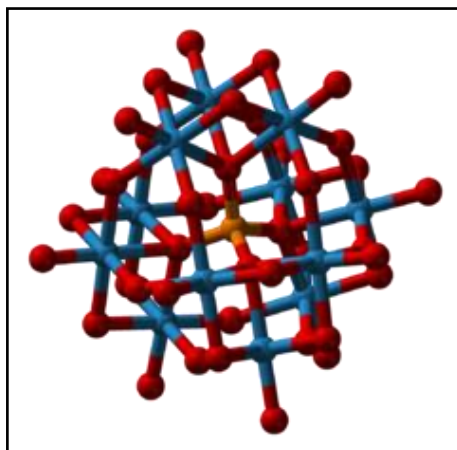
Figure 3.6 Structure of the phosphotungstate anion [45]

(yellow circle: P, blue circles: W, red circles: O)

Silicotungstic acid (STA) is another well-known heteropoly acid. Its molecular formula is $H_4[W_{12}SiO_{40}]$ where silicon is the hetero atom and tungsten is the addenda atom and the structure is Keggin structure. This compound is also known as tungstosilisic acid [46].

Phosphomolybdic acid (PMA) is a yellow-green compound which is soluble in water and polar organic solvents. Its molecular formula is $H_3PMo_{12}O_{40}$ where phosphorus is the hetero atom and molybdenum is the addenda atom and the structure is Keggin structure. It is also known as molybdophosphoric acid and dodecamolybdophosphoric acid [47].

Silicomolybdic acid is another heteropoly acid with the molecular formula of $H_4[SiMo_{12}O_{40}]$ where silicon is the hetero atom and molybdenum is the addenda atom and its structure is Keggin structure [48].

HPAs represent better (Brønsted) acidity than traditional solid acid catalysts such as acidic oxides and zeolites. The acid sites in HPA are more uniform and easier

to control than those in other solid acid catalysts. When the well-known Keggin HPAs are examined, it is seen that the acid strength increases in the order: SMA<PMA<STA<TPA [49]. However, HPAs have low thermal stability; therefore, they have restricted reaction temperature and have decoking problem which is regeneration of solid HPA catalysts. The thermal stability of Keggin HPAs increases in the order: SMA<PMA<STA<TPA. When acidity and thermal stability are compared, it is seen that the strongest acid, TPA, also shows the best thermal stability [50].

Heteropolyanions with different structures than the Keggin can be produced. Examples of these structures are Wells-Dawson, Anderson-Evans-Perloff, Dexter, and so on. [44]. These structures are given in Figure 3.7. However, HPAs with other structure types are less stable than Keggin structure [51]. Generally, tungsten HPAs are the best choice as catalysts because they have better acidity than molybdenum HPAs. Also, they have higher thermal stability and lower oxidation potential [49]. As a result of these properties, tungstophosphoric acid (TPA) is the most widely studied for acid catalysis.
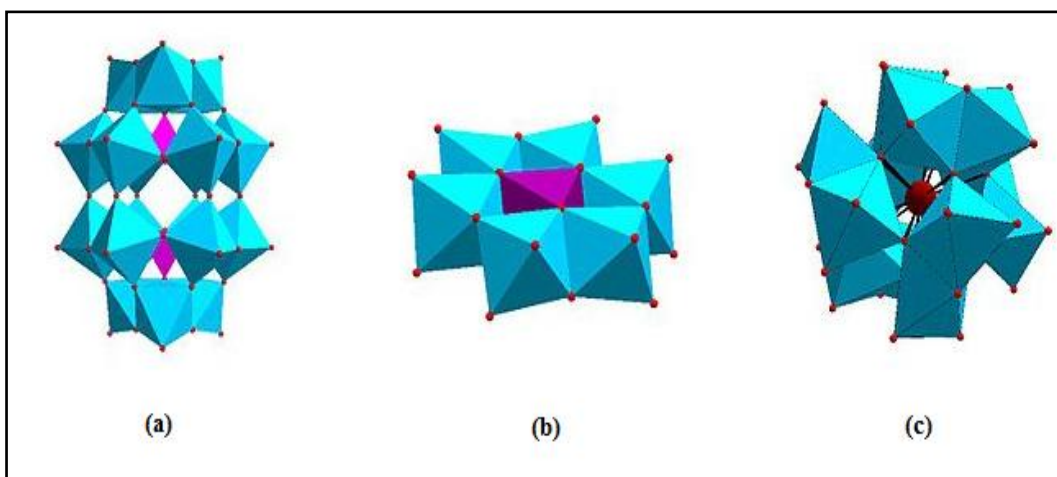
Figure 3.7 (a) Wells-Dawson Structure, (b) Anderson Structure,
(c) Dexter Structure [44]

Anionic charge of heteropolyacids is the key factor when determining the relative acid strength. In general, the acid strength increases with a decrease in the charge of a conjugate base and so with an increase in the stability. Therefore, TPA has the strongest acidity among the Keggin family of heteropolyacids due to the lowest negative charge of the $PW_{12}O_{40}^{-3}$ anion [52]. However, acid strength is not enough to be used as catalysts. Surface area of the material is also important and HPAs have surface areas in the solid state lower than 10 m^2/g. This resulted in a limitation in the use of HPAs as catalysts. In order to increase the surface area of the HPAs, they are supported on a high surface area carrier. Appropriate carriers must have asidic properties in order to prevent the HPA react with the surface. Examples for this kind of materials are silica, zirconia polymers and siliceous MCM-41 materials [53].

In this study, TPA is selected for the modification of SBA-15 because of its higher acidity and thermal stability which makes it the best selection as a catalyst [54].

CHAPTER 4

LITERATURE SURVEY

As plastics gain much interest in recent years and begin to be used in household and the industry, disposal of these plastics became an important environmental problem. Chemical degradation of these polymers is a successful method to the solution of this problem. In this method, plastics are degraded into gases and liquids which can be further used as petrochemical feedstock. There are two ways to apply this method and these are the non-catalytic and catalytic thermal degradation. The catalytic degradation is preferable than the non-catalytic degradation because using acidic catalysis for this purpose decreases the reaction temperature and gives high quality products. In the recent years, acidic mesoporous catalysts have been used in polymer degradation reactions. Studies about the non-catalytic and catalytic thermal degradation of polymers are summarized below.

Obalı et al. [55] studied the catalytic degradation of polypropylene using thermal analyzer and for this purpose, synthesized well-ordered mesoporous SBA-type catalysts in different aluminum ratios and from different aluminum sources. From XRD patterns of these catalysts which were synthesized using aluminum isopropoxide as the aluminum source, it was observed that the main peak of SBA-15 was deformed due to the structural irregularity. On the other hand, the well-ordered structure of SBA-15 did not deteriorate too much when aluminum level was low when aluminum sulphate used as the aluminum source. All the synthesized catalysts showed Type IV isotherms with a H1 hysteresis loop and they have high surface areas. TEM images of SBA-type materials showed well-

ordered hexagonal arrays of uniform mesopores with channels. The pore structure of the material was in honeycomb form that is common for mesoporous materials. The Brønsted acid sites were much stronger than Lewis acids in the aluminum loaded SBA-type catalysts synthesized using aluminum sulphate. The TGA results showed that aluminum containing SBA-type catalysts decreased the reaction temperature and caused a significant decrease in the activation energy of the reaction from 172 kJ/mol to a value in the range of 51–89 kJ/mol depending on the amount of aluminum loading.

Aydemir et al. [56] studied the synthesis of thermally stable, well ordered TPA containing mesoporous SBA-15 materials having different W/Si ratios. TPA was incorporated into the framework hydrothermally synthesized SBA-15 material. Materials showed Type IV isotherm and had a surface area range of 212-825 m^2/g. Also the pore diameters of these materials showed their mesoporosity. The main peak of TPA was observed in the XRD results. Hexagonal and honeycomb structure was seen in the SEM and TEM images. DRIFTS results showed the formation of Brønsted acid sites after including TPA. TPA-impregnated SBA-15 materials showed an important decrease in the degradation temperature of polyethylene and decreased the activation energy values for the polyethylene degradation reaction decreased from 136 kJ/mol to 62-74 kJ/mol depending on the TPA amount.

Walendziewski [57] studied waste polymer (PE, PS, PP and their mixtures) cracking reactions in two different sets of experiments. The first set of experiments were carried out in a glass reactor under atmospheric pressure and in the temperature range of 350-420°C and the second set was carried out in autoclaves under hydrogen pressure and in the temperature range of 380-440°C. As a result of these experiments, it was observed that using alkaline catalyst as cracking catalyst lowers the reaction temperature and the density of the liquid products. Also, increases the gas product yield but has no effect on gas composition. When the two sets were compared, it was observed that the experiments carried out in an autoclave, at long contact time and high

temperature, resulted in larger conversion level, larger gas and gasoline fraction yields.

Xie et al. [58] synthesized MCM-41 modified by Mo and Zr and studied catalytic cracking of polypropylene (PP) over this catalyst. These results revealed that Zr–Mo-MCM-41 showed high activity for the cracking of PP and good selectivity for producing liquid hydrocarbons of higher carbon numbers (C_4-C_{16}). Mo increases the selectivity to high carbon number hydrocarbons and Zr increases the acidity of catalyst and results in the increasing cracking conversion of PP.

Achilias et al. [59] studied the chemical recycling of LDPE, HDPE and PP using both a dissolution/reprecipitation technique and pyrolysis. The first leads to high recovery of polymer with the disadvantage of using large amounts of organic solvents and it was found that the product recycled is almost identical to the beginning polymer. Furthermore, pyrolysis was investigated as a promising technique for thermochemical recycling of these polymers. In this investigation, results are presented on the catalytic pyrolysis of model LDPE, HDPE and PP using an acid FCC catalyst, and on waste products based on these polymers. The oil and gaseous fractions recovered presented a mainly aliphatic composition consisting of a series of alkanes and alkenes of different carbon numbers with a great potential to be recycled back into the petrochemical industry as a feedstock for the production of new plastics or refined fuels.

Donaj et al. [60] studied catalytic pyrolysis at 500°C and 650°C using 1% of Ziegler-Natta catalyst and only the non-catalytic pyrolysis at 650°C and 730°C. These results showed that higher pyrolysis temperature resulted in the production of lighter hydrocarbons and using a catalyst affected the product distribution in a good way. In the non-catalytic pyrolysis, at 650°C gas and liquid product ratios were 36.9 and 48.4 wt% and at 730°C 42.4 and 44.7 wt%, respectively. In catalytic pyrolysis, at 500°C gas and liquid product ratios were 6.5 and 89.0% wt. and at 650°C 54.3 and 41.9 wt%, respectively.

Kaminsky et al. [61], studied the catalytic pyrolysis of polypropylene by using Lewis acids like $AlCl_3$ and mixtures of Lewis acids and Ziegler-Natta catalysts ($AlCl_3$ and $TiCl_4$). Experiments were carried out both in batch and fluidized bed reactor. Both the use of $AlCl_3$ and mixture of $AlCl_3$ and $TiCl_4$ decreased the reaction temperature. Catalyst amount used in these reactions was between 0.1 and 5 wt % of the polypropylene amount. The non-catalytic thermal degradation temperature is 500°C and it could be decreased to 300°C when the catalyst is used. Also, the presence of the catalyst increased the selectivity of C_4 hydrocarbons instead of longer chain hydrocarbons. It also causes an increase in the light oil fraction and gaseous products.

Chaianansutcharit et al. [62], studied the degradation of PP and PE into liquid hydrocarbons at temperatures of 380 and 430°C, respectively. Pure hexagonal mesoporous silica (HMS) and aluminum-containing HMS (Al-HMS) catalysts were used. The non-catalytic and catalytic degradations of both PP and PE were performed in liquid-phase-contact (LPC) and vapor-phase-contact (VPC) modes. In the liquid-phase-contact PP, and PE pellets melted and reacted directly with active sites of catalyst in the degradation reactor before entering the cracking reactor, however, in vapor-phase-contact PP, and PE were first transformed to volatile organic compounds in the degradation reactor before moving to the cracking reactor where a catalyst was placed. The degradation rates and product yields obtained from degradation of both PP, and PE over HMS catalyst in LPC and VPC were similar to those from thermal reaction, indicating pure silica HMS catalyst has no catalytic activity for degradation of polyolefinic plastics. For Al-HMS catalysts, the degradation rates of PP into liquids in LPC depended upon aluminum content. The higher the aluminum content, the faster the degradation rates and the higher the liquid yields. The liquid products obtained were predominant in C_5–C_{12}. For degradation in VPC, increase in aluminum content and temperature of cracking reactor reduced the liquid product yields and promoted the gaseous products, whereas, the residues were controlled by the thermal degradation in the degradation reactor.

Peterson et al. [63], studied the thermal degradation of PS, PE and PP under both inert nitrogen and air atmospheres using thermogravimetry and DSC. The model-free isoconversional method was used to calculate activation energies as a function of the extent of degradation. The dependencies are evaluated in terms of degradation mechanisms. Under nitrogen, the non-catalytic thermal degradation of polymers follows a random scission pathway that has an activation energy of ~200 kJmol^{-1} for PS, 240 kJmol^{-1} for PE and 250 kJmol^{-1} for PP. Lower values (~150 kJmol^{-1}) are observed for the initial stages of the thermal degradation of PE and PS; this suggests that degradation is initiated at weak links. In air, the thermoxidative degradation occurs via a pathway that involves decomposition of polymer peroxide and exhibits an activation energy value of 125 kJmol^{-1} for PS and 80 and 90 kJmol^{-1}, for PE and PP respectively.

Takuma et al. [64], studied the catalytic and non-catalytic degradation of LDPE, HDPE and PP in a fixed-bed flow reactor system. As a catalyst H-gallosilicate was used. Reaction temperature was selected between 375 and 550°C to examine the product distribution and catalyst stability. When gallosilicate was used as a catalyst in catalytic degradation, lighter hydrocarbon mixtures which were rich in valuable aromatic components (mainly benzene, toluene, and xylenes) were produced. Structure of the polymers slightly affects the product distribution because the catalytic degradation of polyolefins passes through similar intermediates regardless of the structure of the polymers, leading to almost the same product distributions. When reused, the gallosilicate showed a stable catalytic activity for the degradation of polyolefins because a very small amount of coke was accumulated on its surface.

Sakata et al. [65], studied degradation of plastic polymers with and without catalysts in a batch reactor at temperatures 430°C and 380°C for PE and PP, respectively. These catalysts were acid-catalysts, zeolite and non-acidic mesoporous silica catalysts. The results of catalytic degradation experiments were compared with the results of non-catalytic thermal degradation experiments in terms of the amount of gas, liquid products and residues, recovery rates and

boiling point distributions of liquid products. For PP degradation in liquid phase contact with silica-alumina, the yield of liquid hydrocarbons was obtained with 69 wt %, and the boiling point of the oil ranged between 36 and 270°C, equivalent to the boiling point of normal paraffins n-C_6 to C_{15}. The liquid products from catalytic degradation have a carbon number distribution very similar to commercial automobile gasoline. Catalysts processing strong acid sites such as ZSM-5 speeded up the degradation of PP and PE and increased the gas production while decreasing the amount of liquid products. For FSM, which processes no acid sites, the initial rates of PP and PE degradation into liquid were as fast as that over an acid catalyst (silica-alumina) and the liquid yields were higher.

Uemichi et al. [66], studied the degradation of PP to aromatic hydrocarbons. Pt or Fe containing activated carbon is used as catalysts. This study was compared with a similar study which studied the degradation of PE and the results showed that they were essentially the same. The mechanism seems to be applicable to the degradation of other polyolefins, taking into account the structure of the decomposed fragments. The presence of methyl branching in the polymer structure was unfavorable for the formation of aromatics not only over metal-free activated carbon but also over the Pt- and Fe-containing catalysts. Further, the added Pt was found to induce some ring expansion activity in the catalyst, while the addition of Fe had no effect on the activity.

The Objective of the Study:

Throughout the literature survey, it was observed that there are very few studies on catalytic degradation of polypropylene which uses tungstophosphoric acid loaded SBA-15 materials as catalysts. For this reason, the objective of this study is:

- To synthesize tungstophosphoric acid loaded SBA-15 hydrothermally at different TPA loadings,

- To characterize these catalysts,

- To test the performances of these catalysts in TG analyzer,

- To determine the kinetic parameters of polypropylene degradation reaction using thermogravimetric analysis data.

CHAPTER 5

EXPERIMENTAL METHOD

The experimental study is based on three main parts: the first part is the synthesis of catalysts, the second part is characterization of the synthesized catalysts using X-Ray Diffraction, Nitrogen Adsorption-Desorption, Scanning Electron Microscopy and Fourier Transform Infrared Spectroscopy and the third part is testing the performance of these catalysts in degradation reaction using thermogravimetric analyzer.

5.1 Synthesis of TPA Loaded SBA-15 Materials

Tungstophosphoric acid (TPA) loaded SBA-15 material was synthesized using a hydrothermal synthesis method. Firstly, 4 g of surfactant, which is triblock copolymer poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) (Sigma-Aldrich Co.), was added to 120 mL of 2M HCl solution and stirred for 4 h at $40^{o}C$ with a mixing rate of 350 rpm in order to dissolve the surfactant. At the end of 4 hours, while the mixing of solution continues, 8 g of silica source, tetraethyl orthosilicate (TEOS) (Merck), was added dropwisely into it. TPA is added 30 min after TEOS addition. Before adding it to the solution, TPA is dissolved in 2 mL of deionized water. Amount of TPA is different in all samples and the calculation of TPA amount is given in Appendix A. Likewise TEOS, TPA is added dropwisely to the solution while the mixing of solution continues and the solution kept stirred for 24 h. At the end of the stirring period, the final solution was transferred into a teflon-lined stainless steel autoclave for the hydrothermal

synthesis at a temperature of 100°C for 48 h. Then the mixture was filtered and washed with deionized water. Finally, the obtained product was dried in the oven at 80°C for 24 h and calcined in a tubular furnace at 500°C for 8 h with a flow of dry air in order to remove organic materials within the pores of the catalyst. This procedure is given schematically in Figure 5.1.

The synthesized TPA loaded SBA-15 materials were named as SBA15-TPAX where X stands for the ratio of W/Si. For example, when W/Si ratio is 0.10, the sample is named as SBA15-TPA0.10.
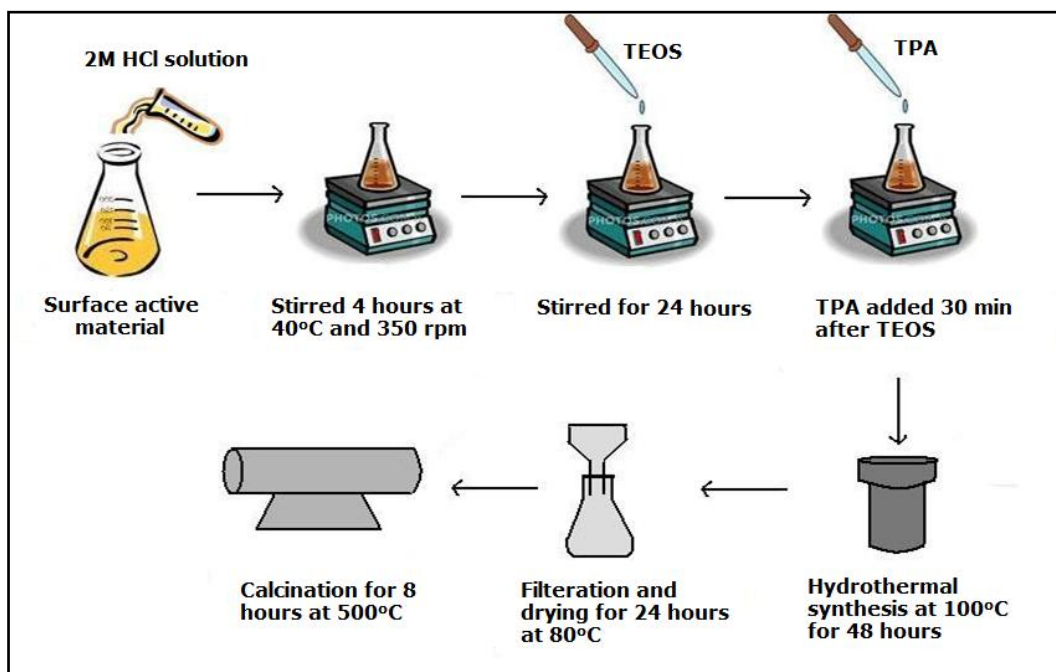

Figure 5.1 Scheme of hydrothermal synthesis route for TPA loaded SBA-15 material

5.2 Characterization Techniques for the Synthesized Catalysts

Physical and structural properties of the synthesized materials were determined using the following techniques: X-Ray Diffraction, Nitrogen Adsorption-Desorption, Scanning Electron Microscopy and Fourier Transform Infrared Spectroscopy.

5.2.1 X-Ray Diffraction

Synthesized materials were analyzed using X-Ray Diffraction method in order to get information about the crystallinity and regularity of the structure. Both low angle (0.8°-10°) and wide angle (0.8°-80°) analysis were performed. The equipment used in the low angle analysis was Rigaku D/MAX2000 Diffractometer and the equipment used in the wide angle analysis was Rigaku Ultima-IV Diffractometer. The step size in both analyses was 0.02. Voltage and current were 40 kV and 30 mA in low angle analysis and 40 kV and 40 mA in wide angle analysis.

5.2.2 Nitrogen Adsorption-Desorption

Physical properties of the synthesized materials, such as surface area, pore diameter, pore volume and pore size distributions were determined by nitrogen adsorption technique. Multipoint BET surface area, adsorption-desorption isotherms and average pore size of the samples were measured using Quantachrome Autosorb-1C/MS equipment. The samples were degassed at $120^{o}C$ overnight before the analysis. The analyses were performed at a relative pressure range of 0.05 to 0.99 at liquid nitrogen temperature.

5.2.3 Scanning Electron Microscopy

Morphology of the catalysts was analyzed using the QUANTA 400F Field Emission Scanning Electron Microscope. Before the analysis, the samples were prepared. First, a small double-sided sticky carbon tape was attached onto the metal apparatus of the machine. Secondly, a small amount of sample was put onto this carbon tape and it was spread to the surface of the tape homogeneously. Lastly, the samples were coated with gold and palladium under high vacuum conditions in order to prevent pushing of electrons because during SEM analysis, electrons are sent to the sample and if sample loaded with too much electrons, it pushes the new electrons. Gold and palladium coating is conductor and therefore prevents electron pushing.

5.2.4 Fourier Transform Infrared Spectroscopy

In order to observe the acid sites of the synthesized materials, FTIR analysis was carried out using Perkin Elmer-Spectrum One FTIR spectrometer in the wave number range of 400-4000 cm^{-1}. DRIFTS analysis of the fresh catalysts and pyridine adsorbed catalysts were performed using the same equipment. Before the analysis of the pyridine adsorbed samples, 2 ml of pyridine was added to 0.0050 g of the sample and kept under the hood overnight to allow pyridine to be evaporated. Then, all the samples were mixed with potassium bromide (KBr) in a weight ratio of 1:20. Before performing the analysis of the samples, a background spectrum of pure KBr was taken and then, the samples which were prepared with and without pyridine were analyzed. In order to obtain the spectra giving information about the acid sites within the synthesized material, the spectra of pyridine adsorbed sample was subtracted from the spectra of pyridine free sample.

5.3 Thermogravimetric Analysis

Thermogravimetric analysis was carried out in order to test the performance of the synthesized catalysts in the degradation reaction of polypropylene. The polymer was polypropylene (Aldrich Co.) of molecular weight 250000, density 0.9 g/ml, melt index 12.00 g/10 min and melting point 160-165°C. These experiments were performed under nitrogen atmosphere with a flow rate of 60 cc/min and heating rate of 5°C/min and in the temperature range of 30-550°C.

Two types of experiments were performed. Firstly, samples were prepared with different catalyst to polypropylene ratios using same catalyst. For this purpose 20% TPA loaded SBA15-TPA0.20 catalyst was used with catalyst/PP ratios of 1/2, 1/5, 1/10. Secondly, samples were prepared using all catalysts with a fixed catalyst/PP ratio of 1/2.

CHAPTER 6

RESULTS AND DISCUSSION

In this study, TPA loaded SBA-15 catalysts were synthesized with a hydrothermal method and these catalysts were characterized using X-Ray Diffractometer (XRD), Nitrogen Physisorption method, Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). Also, their activity in the polypropylene degradation reaction was tested using Thermal Gravimetric Analyzer (TGA).

6.1 Characterization Results of the Synthesized Materials

6.1.1 X-Ray Diffraction Results of the Synthesized Materials

XRD patterns of TPA containing SBA-15 materials at the low Bragg angle are shown in Figure 6.1. The main peak of TPA loaded was at the Bragg angle value of 0.84°. Secondary peak was observed at 2Ө value of 1.44°. Tertiary peak at 1.72° combined with the secondary peak. The main, secondary and tertiary peaks are indexed to (100), (110) and (200) reflections of ordered hexagonal mesophase, respectively and the patterns of the synthesized materials match well with the pattern of the ordered mesoporous SBA-15 [67].
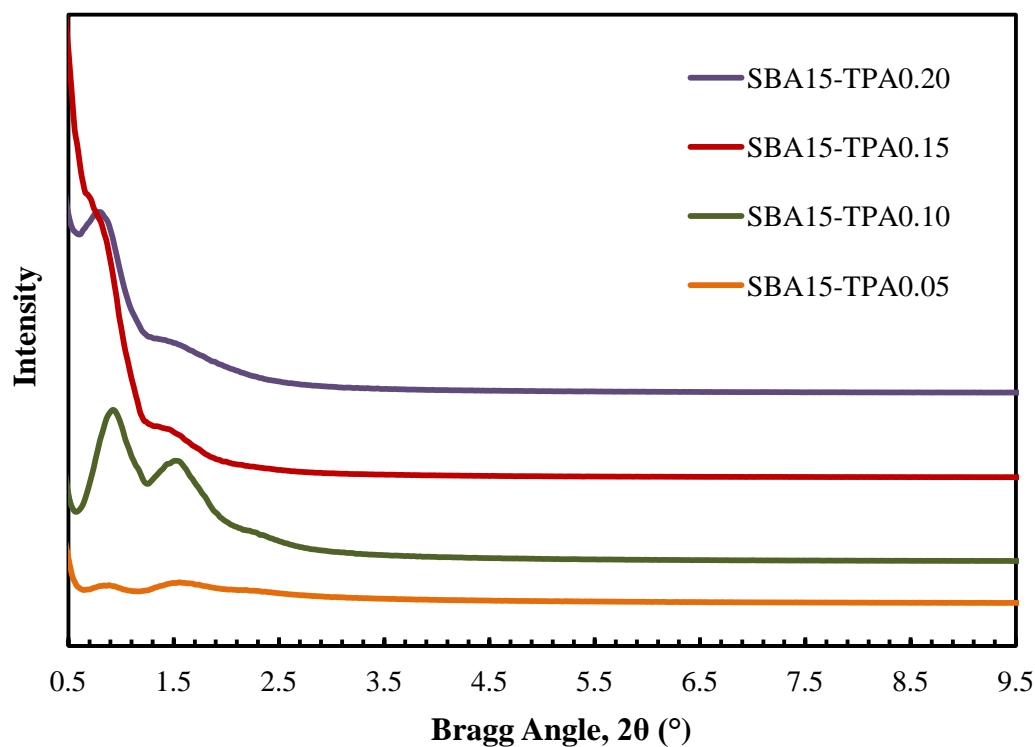
Figure 6.1 Low angle X-Ray Diffraction patterns of TPA loaded SBA-15 materials

In Figure 6.2, wide angle X-Ray diffraction patterns of TPA loaded materials are given. A broad peak at a Bragg angle value of 24° was observed in both of these materials corresponding to the amorphous structure of silica [56]. The X-Ray Diffraction pattern of pure TPA is given in Appendix B and the characteristic peaks of TPA were at 2Ө values of 8.07 and 8.84. In SBA15-TPA0.10 and SBA15-TPA0.20 samples, these peaks were not observed. XRD results showed that TPA dispersed well in the structure, did not cause deformations in the ordered structure of the material.
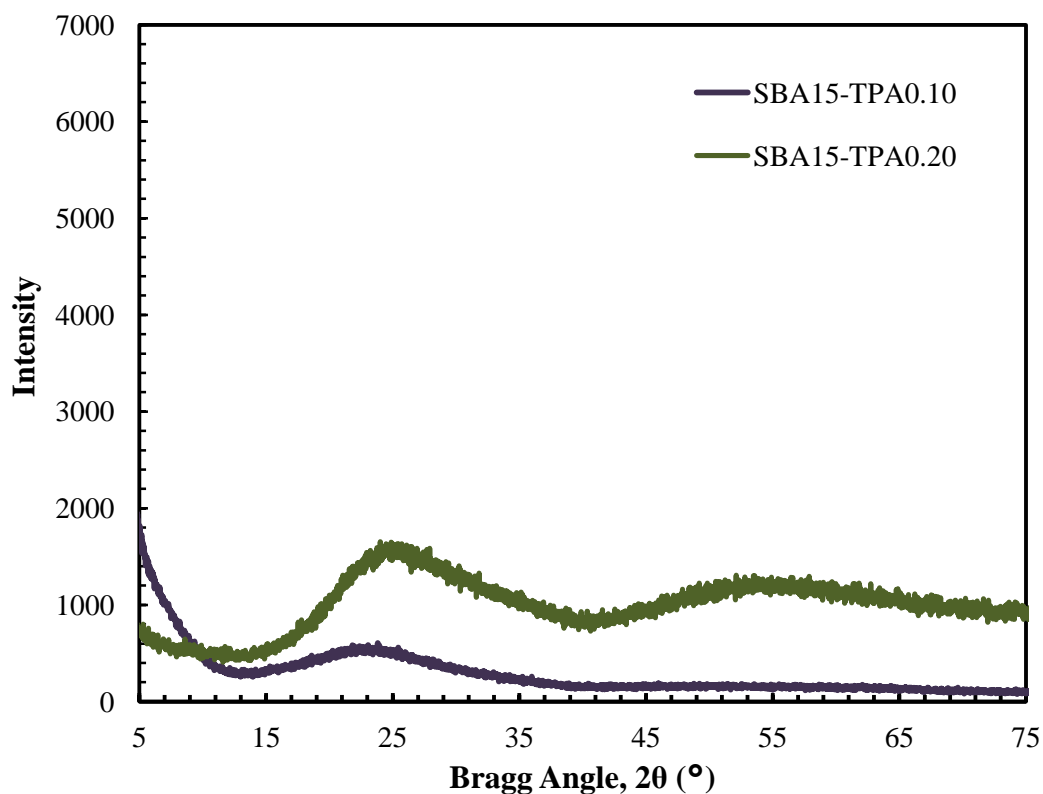
Figure 6.2 Wide angle X-Ray Diffraction patterns of TPA loaded SBA-15 materials

6.1.2 Surface Characterization Results of the Synthesized Materials

Nitrogen adsorption-desorption isotherms of synthesized TPA loaded SBA-15 materials are shown in Figure 6.3. According to the IUPAC classification, the synthesized materials exhibited isotherms of Type IV, which is a typical of mesoporous material. While adsorption/desorption are in the same mechanism in microporous materials, these two physical events take place following different pathways in mesoporous materials. Therefore, hysteresis formation is observed due to the capillary condensation of N_2 in the mesopores of the structure [26]. The synthesized materials except for SBA15-TPA0.20 showed H1 hysteresis which indicates narrow pore size distribution and SBA15-TPA0.20 showed H2

hysteresis. When the hysteresis shifts to right, pore diameter becomes larger. From Figure 6.3, SBA15-TPA0.10 and SBA15-TPA0.15 materials are expected to have larger pore sizes and from Table 6.1 it can be seen that these materials have larger pore sizes than SBA15-TPA0.05 and SBA15-TPA0.20. Hysteresis starts at approximately 0.65 relative pressure. With high TPA loading, the adsorbed nitrogen volume significantly decreased. This might be due to the filling or blocking of the micropores and mesopores of SBA-15 materials with TPA species.
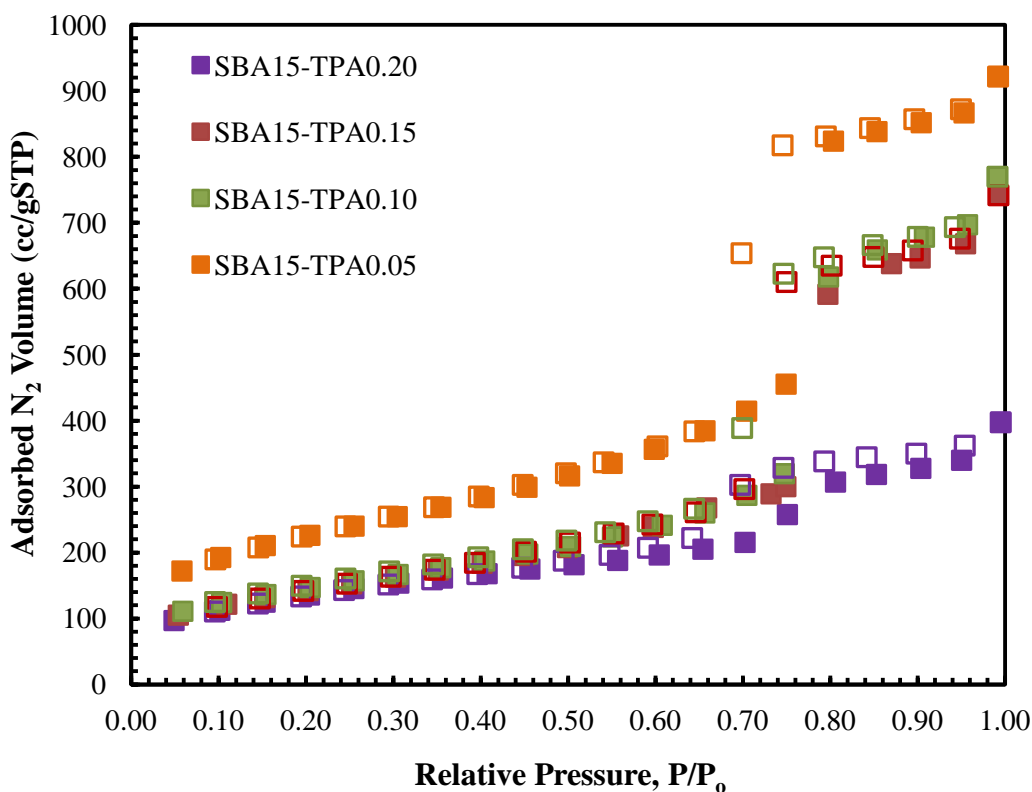

Figure 6.3 Nitrogen adsorption and desorption isotherms of the synthesized materials (solid boxes: adsorption branch, blank boxes: desorption branch)

In Table 6.1, BET surface area, pore volume and pore diameter values of the samples are tabulated. Incorporation of TPA to the silica at high loading above 0.05 of W/Si ratio caused a sharp decrease in the surface area values. This sharp decrease might be due to the location of TPA species on the walls of SBA-15. Pore diameters which were calculated using BJH model (Table 6.1) are in the range of 65 to 78 Å. This indicates the mesoporosity of the material, as expected.

Table 6.1 Surface area and pore size values of the synthesized materials

Sample	Surface Area Multipoint BET (m^2/g)	Pore Volume (BJH Des.) (cc/g)	Average Pore Diameter (nm)
SBA15-TPA0.05	786	1.41	6.5
SBA15-TPA0.10	516	1.21	7.7
SBA15-TPA0.15	507	1.17	7.8
SBA15-TPA0.20	478	0.59	6.5

In Figure 6.4, pore size distributions of the synthesized materials obtained using BJH model are given. For all samples, pore size distribution shows a pore diameter range of 50 to 100 Å, which is again an indication of the mesoporous structure [68]. Also, the shift to the right means that average pore diameters are not same therefore; the result of Figure 6.4 is consistent with the results in Table 6.1. Pore volume decreased as the amount of TPA loading increased. This might be due to the fact that TPA species filled or blocked the micropores and mesopores of SBA-15 materials. These results were consistent with nitrogen adsorption-desorption isotherm results (Figure 6.3).
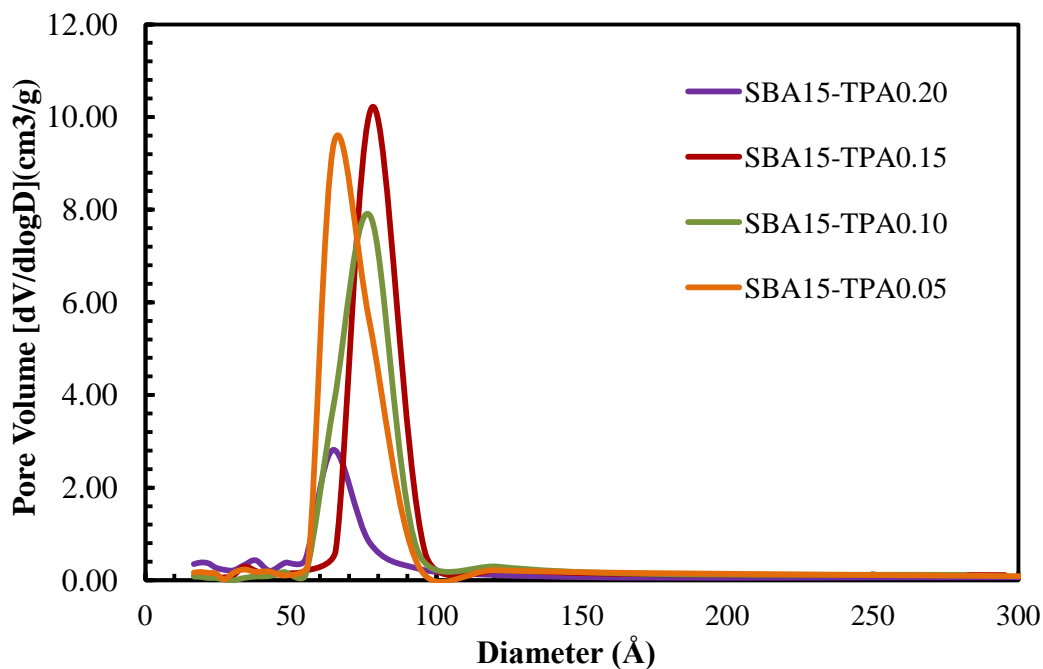
Figure 6.4 Pore size distributions of the synthesized materials

6.1.3 Scanning Electron Microscopy Results

Morphologies of the synthesized materials were observed by Scanning Electron Microscopy analysis. The images of the synthesized materials are given in Figure 6.5-6.8 and as seen from these images, TPA loaded SBA-15 materials showed same properties with purely synthesized SBA-15 [56]. These images showed that particles of the synthesized materials have a hexagonal structure. Also, agglomerations were observed in the material when TPA was loaded into the structure of the SBA-15 material. TPA addition did not cause a variation in the shape of the particles.

Average particle sizes are measured from the images and it was observed that as TPA amount loaded to the materials were increased, the particle sizes were became larger. The average particle sizes were calculated choosing around 20

particles from the figures and found as 0.57 µm for SBA15-TPA0.10 material (Figure 6.6) and 0.81 µm for SBA15-TPA0.15 material (Figure 6.7).
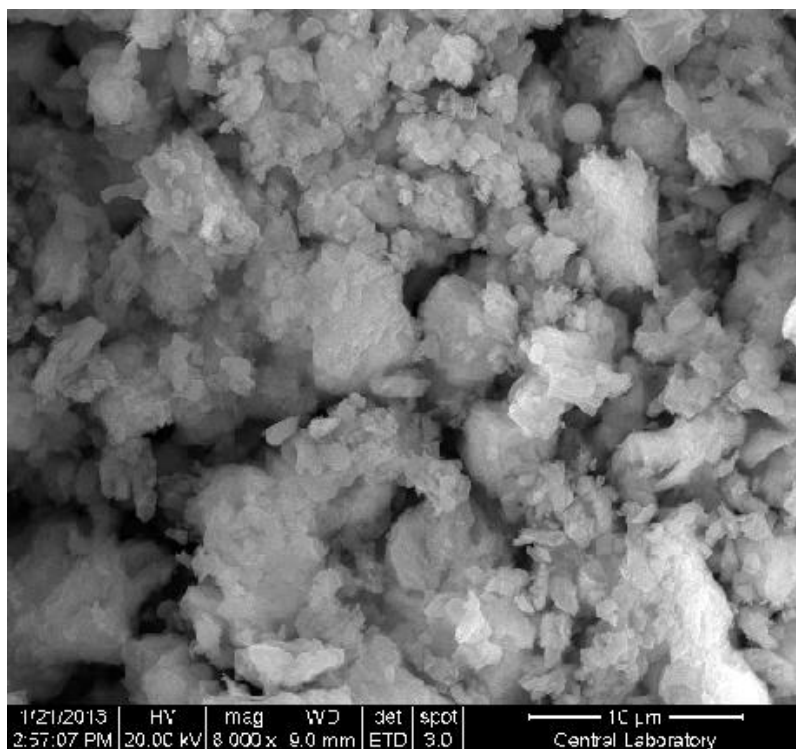

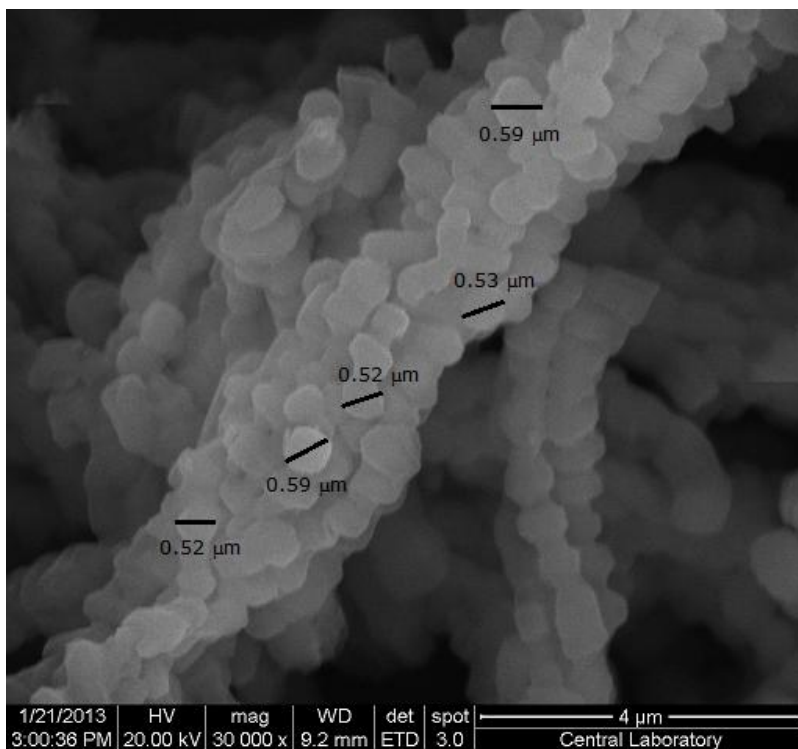**Figure 6.5** SEM image of SBA15-TPA0.05 material at 8000x magnification

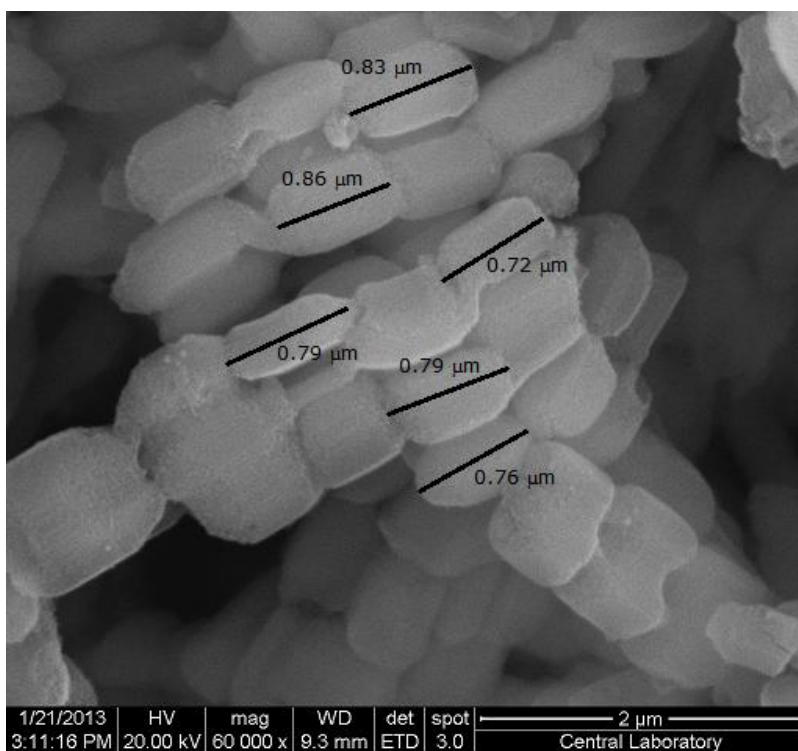**Figure 6.6** SEM image of SBA15-TPA0.10 material at 30000x magnification

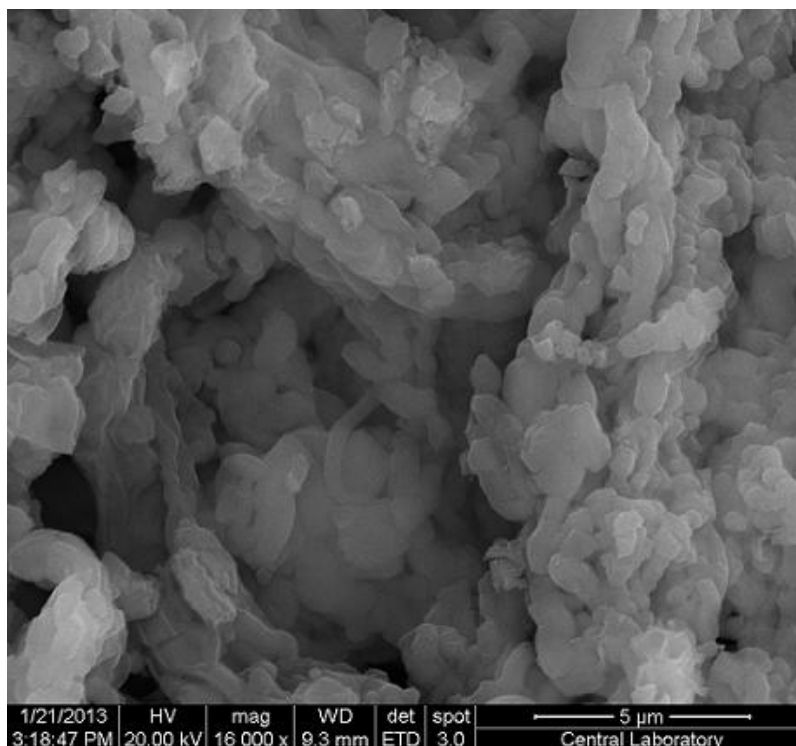**Figure 6.7** SEM image of SBA15-TPA0.15 material at 60000x magnification

Figure 6.8 SEM image of SBA15-TPA0.20 material at 16000x magnification

6.1.4 Fourier Transform Infrared Spectroscopy Results

FTIR spectra of fresh catalysts are given in Figure 6.9. The peaks that showed up at 806 cm^{-1}, 889 cm^{-1}, 967 cm^{-1}, and 1070 cm^{-1} are the characteristic peaks of tungstophosphoric acid [69]. The bands at 806 cm^{-1} and 889 cm^{-1} are because of the W-O$_c$-W and W-O$_b$-W stretching vibrations. Subscripts b and c signifies the oxygen binding to tungsten (WO$_6$) by corner-sharing and edge sharing, respectively [70]. The band at 967 cm^{-1} is due to W=O and the band at 1070 cm^{-1} is due to the P-O in the central tetrahedron [67]. Band at around 1070 cm^{-1} with a shoulder at 1200 cm^{-1} is because of the asymmetric Si-O-Si stretching vibrations and this peak overlaps with P-O vibration peak [71]. The band occurs at around 798 cm^{-1} is because of the Si-O-Si symmetric stretching and this peak overlaps with W-O$_c$-W stretching vibration peak [39]. Therefore, only TPA peaks distinguishable in the spectra of the synthesized materials are the peaks observed

at 889 cm^{-1} and 967 cm^{-1}. The TPA peaks at 806, 967 and 1070 cm^{-1} are detectable in the spectra of the synthesized materials. Detection of these peaks showed that TPA incorporated into the structure of SBA-15.

The broad band that showed up at a maximum of 3450 cm^{-1} is due to the surface silanol groups and adsorbed water [72]. The peak observed at 1612 cm^{-1} is due to the bending vibration of adsorbed water [73]. The band that showed up at 3748 cm^{-1} is due to the presence of free Si-OH (silanol) groups in the synthesized materials [73]. The band obtained at 3748 cm^{-1} decreased as the amount of TPA loaded increased because in higher loadings more TPA is bonded to these silanol groups.
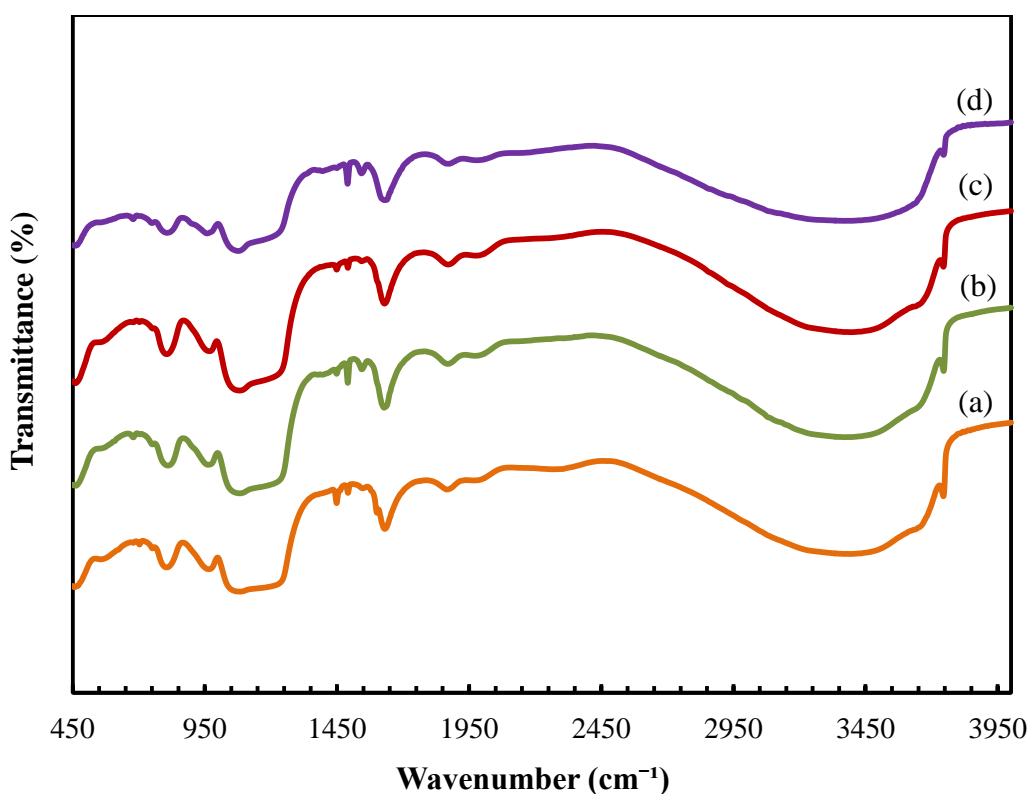

Figure 6.9 FTIR spectra of the fresh catalysts: (a) SBA15-TPA0.05, (b) SBA15-TPA0.10, (c) SBA15-TPA0.15, and (d) SBA15-TPA0.20

Presence of Lewis and Brønsted acid sites in the TPA loaded samples were observed by adding pyridine on the materials. When pyridine adsorbed on the materials, the DRIFTS spectra become different from the fresh catalysts. With the help of this difference, the characteristic peaks that give information about Lewis and Brønsted acid sites in the TPA loaded materials can be seen.

In Figure 6.10, the DRIFTS spectra of the difference between pyridine adsorbed and fresh catalysts are shown. The band at 1448 cm^{-1} is due to the Lewis acidity, and the band at 1540 cm^{-1} is due to Brønsted acidity and the band at 1489 cm^{-1} due to both Lewis and Brønsted acid sites in the structure [43]. When SBA-15 synthesized without any loading, only Lewis acid sites are exist in the structure [56]. When TPA is hydrothermally loaded into SBA-15, Brønsted acid sites occured in the structure and as the amount of TPA increased, the intensities of the peaks regarding to Brønsted acidity were increased. However, SBA15-TPA0.10 showed a better peak intensity than SBA15-TPA0.15 which means that 10% TPA loaded samples had a better acidity than 15% loaded samples. When the Brønsted and Lewis peak intensities were compared using Figure 6.10, it was observed that for SBA15-TPA0.20, Brønsted intensity is 2 times the Lewis intensity. This ratio is 0.5, 1.5 and 0.13 for SBA15-TPA0.15, SBA15-TPA0.10 and SBA15-TPA0.05, respectively.
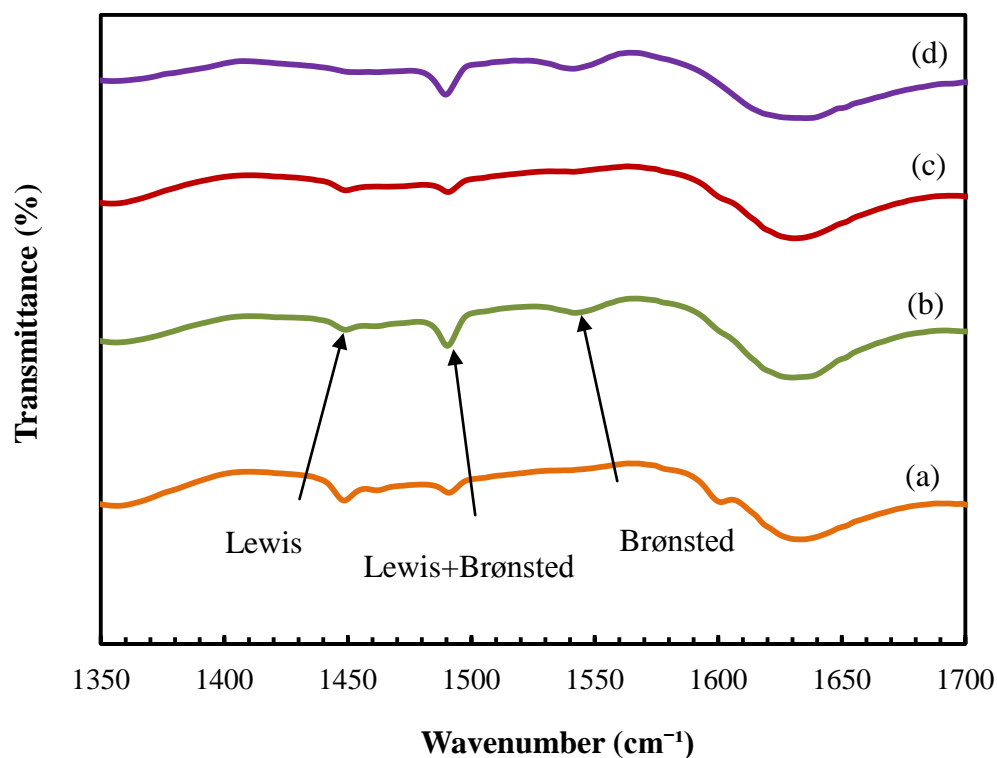
Figure 6.10 DRIFTS spectra of the pyridine adsorbed TPA loaded
SBA-15 catalysts: (a) SBA15-TPA0.05, (b) SBA15-TPA0.10,
(c) SBA15-TPA0.15, and (d) SBA15-TPA0.20

6.2 Thermogravimetric Analysis

6.2.1 Effect of Catalyst Amount on the Polymer Degradation Reaction

Thermogravimetric analysis of the synthesized samples showed the behavior of
the prepared polymer-catalyst mixtures at a given temperature interval. In Figure
6.11, TGA plots of polymer-catalyst mixtures at different weight ratios are given.
As seen in the figure, polypropylene showed a steep weight loss in a specific
temperature interval. This situation occurs because of the chain degradation.
Decomposition temperature shifted to left because chain degradation comes to

lower temperatures when catalyst is used. The reason why chain degradation comes to lower values is the acid sites exists in the catalysts because degradation reaction takes place on the acid sites. When catalyst amount increased, acidity increased and the chain degradation takes place at a lower temperature. Therefore, catalyst to polymer ratio of 1/2 decreased the degradation temperature most.
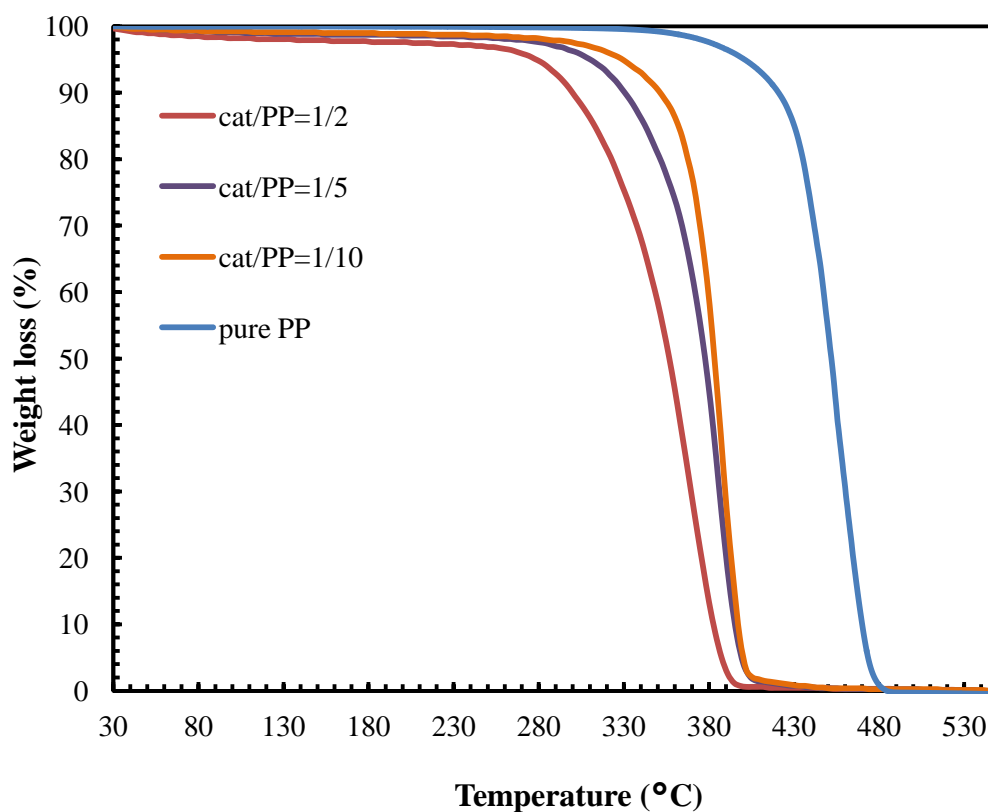

Figure 6.11 TGA plots for comparison of different catalyst/polymer ratios
(Catalyst: SBA15-TPA0.20)

6.2.2 Effect of TPA Amount on the Polymer Degradation Reaction

Figure 6.12 indicates the TG analysis of the polypropylene with the synthesized materials under nitrogen flow. The analysis done with the lowest TPA loaded sample, SBA15-TPA0.05, showed same weight loss behavior with the pure PP. However, temperature range shifted to left with an increase in TPA loading because of the increase in acidity and so the decrease in the chain degradation temperature. As mentioned before, the acid sites introduced to the structure by hydrothermal method had a positive effect on the activity of the catalyst for degradation of PP. Loading higher amount of TPA resulted in the increase in the amount of acid sites, therefore, caused a decrease in the polypropylene decomposition reaction temperature. As mentioned in the FTIR analysis, SBA15-TPA0.10 sample showed a better acidity than SBA15-TPA0.15 sample, therefore, temperature range shifted to a lower value in SBA15-TPA0.10 sample.
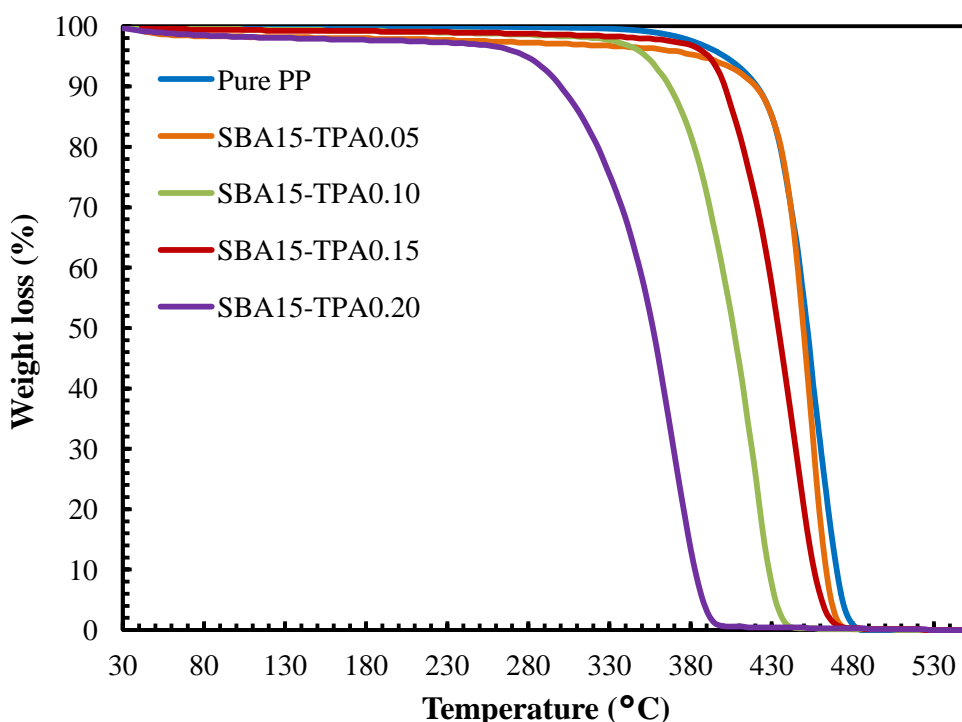

Figure 6.12 TGA plots of tungstophosphoric acid loaded SBA-15 samples

($M_{Catalyst}/M_{Polypropylene}$: 0.5)

6.2.3 Activation Energies of the Synthesized Materials

The activation energy value of the polypropylene cracking reaction was evaluated in the presence of synthesized catalysts using the TGA data following the Simple Power Law rate expression given in Appendix C. The overall order of the PP degradation reaction was found to be 1 for TPA loaded SBA-15 catalysts. The activation energy for the polypropylene degradation reaction in the absence of the catalyst was found to be 172.0 kJ/mole [74]. For TPA loaded samples, activation energy values were between 92.5 and 165.8 kJ/mole (Table 6.2). It was observed that there was a decrease in the activation energy of PP degradation reaction depending on the loading of TPA.

Table 6.2 Activation energies of the degradation reaction calculated for pure polypropylene and catalyst added samples

Sample	Activation Energy (E_A) Values (kJ/mol)
No catalyst	172.0
SBA15-TPA0.05	165.8
SBA15-TPA0.10	156.0
SBA15-TPA0.15	133.4
SBA15-TPA0.20	92.5

TPA loaded SBA-15 catalysts showed good activity in the polymer degradation reaction. Among all TPA loaded SBA-15 materials, SBA15-TPA0.20 reduced the activation energy the most. This was regarded to the increase in the Brønsted acid sites in the structure with more TPA loading amounts.

These results were compared with the literature [74]. In that work, aluminum loaded SBA-15 materials were synthesized with impregnation method and these materials were used in the catalytic degradation of polypropylene. When aluminum was added to SBA-15 with a Al/Si ratio of 0.2, activation energy decreased 70%. However, when TPA was added to SBA-15 with the same ratio, it decreased 20%.

CHAPTER 7

CONCLUSIONS

In this study, TPA loaded SBA-15 materials were hydrothermally synthesized to be used in the degradation reaction of polypropylene. These synthesized materials were characterized using X-Ray Diffractometer (XRD), Nitrogen Physisorption method, Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) and their performances were evaluated using Thermal Gravimetric Analyzer (TGA).

In the wide angle XRD patterns characteristic TPA peaks cannot be observed which means that the synthesized materials showed an amorphous structure and TPA loaded materials did not cause deformations in the regularity.

Nitrogen adsorption and desorption analysis showed that the synthesized materials exhibited Type IV isotherms. The surface area of TPA loaded SBA-15 samples were in the range of 478-786 m^2/g. Pore size distribution of the synthesized materials revealed their mesoporosity. The average pore sizes were in the range of 6.5-7.8 nm depending on TPA loading amount.

SEM indicates that particles of synthesized materials were in the hexagonal structure. TPA addition did not change the shape of the particles and agglomerations were observed in the material when TPA was loaded into the structure of the SBA-15 material.

It can be observed that when TPA was hydrothermally loaded into SBA-15, Brønsted acid sites occurred in the structure and the intensities of the Brønsted acidity peaks increased as the amount of TPA increased.

Activity test results showed that catalyst amount used in the experiments and TPA amount loaded to SBA-15 materials have a positive effect on the polypropylene degradation reaction which means that with an increase in the amounts, the reaction temperature shifted to a lower range. For TPA loaded samples, activation energy values were between 92.5 and 165.8 kJ/mole. As the pure polypropylene degradation reaction has an activation energy value of 172 kJ/mole, it can be said that TPA loaded samples decreased the activation energy of the polypropylene degradation reaction. According to all these results, it can be said that hydrothermally synthesized TPA loaded SBA-15 materials are suitable for the degradation reaction of polypropylene.

During the synthesis, TPA added to the solution 30 min after TEOS and this might have caused formation of the SBA-15 structure before the addition of TPA. To prevent this, TPA may be added to the solution earlier.

REFERENCES

1) Aydemir, B., (2010). *"Synthesis of Mesoporous Catalysts and Their Performance in Pyrolysis of Polyethylene",* MSc Thesis, Middle East Technical University, Ankara, Turkey.

2) Obalı, Z., Sezgi, N. A., Doğu, T. (2009). *"Performance of Acidic MCM-like Aluminosilicate Catalysts in Pyrolysis of Polypropylene"*, Chem. Eng. Comm., 196, p.116-130.

3) Nicholson, J. W., *"The Chemistry of Polymers"*, Royal Society of Chemistry, 2006, Cambridge, UK.

4) Pethrick, R.A., *"Polymer science and technology for Engineers and Scientists"* John Wiley & Sons, 2010, New York, USA.

5) Polymer Explained, http://everything.explained.at/Polymer, last accessed date: 10.08.2012.

6) Challa, G., *"Polymer chemistry: an introduction"*, Ellis Horwood, 1993, New York, USA.

7) Briston, J.H., Gosselin, C.C., *"Introduction to plastics",* Newnes, 1968, Feltham Middlesex, England.

8) Peacock, A.J., Calhoun, A.R., "*Polymer chemistry: Properties and Applications*" Hanser Gardner Publications, 2006, Ohio, USA.

9) Polyethylene, http://en.wikipedia.org/wiki/Polyethylene, last accessed date: 10.08.2012

10) Brydson, J.A., *"Plastic Materials",* Butterworth Heinemann, 1999, Oxford, UK.

11) Ibeh, C.C., *"Thermoplastic Materials: Properties, Manufacturing Methods, and Applications"*, Taylor & Francis Group, 2011, New York, USA.

12) La Mantia, F.P., *"Handbook of plastics recycling"*, Rapra Technology Ltd, 2002, Shropshie, UK.

13) Tripathi, D., *"Practical guide to polypropylene",* Rapra Technology Ltd., 2002, Shropshie, UK.

14) Polypropylene, http://www.3dchem.com/molecules.asp?ID=331#, last accessed date: 10.08.2012.

15) Wikipedia, http://en.wikipedia.org/wiki/File:Isotactic-polystyrene-chain-looking-down-axis-from-xtal-3D-vdW.png, last accessed date: 10.08.2012.

16) Indiamart, http://www.indiamart.com/neetachemicals/poly-propylene-p-p-plastics-polymers.html, last accessed date: 12.01.2013.

17) Wikimedia Commons, http://commons.wikimedia.org/wiki/File:Polyethylene-terephthalate-3D-spacefill.png, last accessed date 11.02.2013

18) El-Fadel, M., Findikakis, A.N., Leckie, J.O., (1997). *"Environmental Impacts of Solid Waste Landfilling"* Journal of Environmental Management, 50, p.1–25.

19) Cheremisinoff, N.P., *"Handbook of solid waste management and waste minimization technologies"*, Butterworth Heinemann, 2003, Oxford, UK.

20) Letcher, T.M., Vallero, D.A., *"Waste: A Handbook for Management"*, Academic Press, 2011, Massachusetts, USA.

21) Engdahl, R.B., Krause, H.H., Miller, P.D., (1973). *"Effluents From The Municipal Incineration of Plastics",* Polymers and Ecological Problems, 3, p.81-92.

22) Aguado, J., Serrano, D.P., Braithwaite, M.J., Hassur, S.M., Papenfuhs, T., Clark, J.H., *"Feedstock Recycling of Plastic Wastes",* Royal Society of Chemistry, 1999, London, UK.

23) Scott, G., (2000). *"Green Polymers",* Polymer Degradation and Stability, 68, p. 1-7.

24) Goodship, V., *"Introduction to plastic recycling ",* Rapra Technology Ltd., 2007, Shropshie, UK.

25) Garforth, A.A., Ali, S., Hernandez-Martinez, J., Akah, A., (2004). *"Feedstock recycling of polymer wastes",* Current Opinion in Solid State and Materials Science, 8, p.419–425.

26) Sing, K.S.W., Everett, D.H., Haul R.A.W., Moscou, L., Pierotti, R. A., Rouquerol, J., Siemieniewska, T., (1985). *"Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity",* IUPAC Pure & App. Chem., 57, No. 4, p.603-619.

27) Ciesla, U., Schüth, F. (1999). "*Ordered mesoporous materials*", Microporous and Mesoporous Materials, 27, p.131-149.

28) Sayari, A. (1996). *"Periodic mesoporous materials: synthesis, characterization and potential applications"*, Recent Advances and New Horizons in Zeolite Science and Technology Studies in Surface Science and Catalysis, 102, p.1-46.

29) Beck, J. S., Vartuli, J.C., Roth, W.J., Leonowicz, M.E., Kresge, C.T., Schmitt, K.D., Chu, C. T-W., Olson, D.H., Sheppard, E.W., McCullen, S.B., Higgins, J.B., Schlenker, J.L. (1992). *"A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates"*, J. Am. Chem. Soc., 114, p.10834-10843.

30) Taguchi, A., Schuth, F., (2005). *"Ordered mesoporous materials in catalysis"*, Microporous and Mesoporous Materials, 77, p.1-45.

31) Güçbilmez, Y., (2005). *"Vanadium and Molybdenum Incorporated MCM-41 Catalysts for Selective Oxidation of Ethanol"*, MSc Thesis, Middle East Technical University, Ankara, Turkey.

32) Di Renzo, F., Fajula, F., (2005). *"Introduction to molecular sieves: Trends of evolution of the zeolite community"*, Studies in Surface Science and Catalysis, 157, p.1–12.

33) Wieslaw J. Roth , James C. Vartuli, (2005). *"Synthesis of mesoporous molecular sieves"*, Studies in Surface Science and Catalysis, 157, p.91–110.

34) Oye, G., Sjöblom, J., Stöcker, M., (2001). *"Synthesis, characterization and potential applications of new materials in the mesoporous range"*, Advances in Colloid and Interface Science, 89-90, p.439-466.

35) Sayari, A., Liu, P., (1997). *"Non-silica periodic mesostructured materials: recent progress"*, Microporous Materials, 12, p.149-177.

36) Memoire Online, http://www.memoireonline.com/05/08/1126/m_etude-3structurale-et-dynamique-de-solutions-de-sucre-confinees54.html, last accessed date 09.01.2013.

37) Kresge, C.T., Leonowicz, M., Roth, W.J., Vartuli, J.C., Beck, J.C. (1992). *"Ordered mesoporous molecular sieves synthesized by a liquidcrystal template mechanism*" Nature, 359, p.710-712.

38) Hatton, B., Landskron, K., Whitnall, W., Perovic, D., Ozin, G.A., (2005). *"Past present and future of periodic mesoporous organosilicas-the pmos",* Acc. Chem. Res., 38, p.305-312.

39) Zhao, D.Y., Feng, J.L., Huo, Q.S., Melosh, N., Fredrickson, G.H., Chmelka, B.F., Stucky, G.D., (1998). *"Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores",* Science, 279, p.548–552.

40) Vinu, A., Murugesan, V., Böhlmann, W., Hartmann, M. (2004). *"An Optimized Procedure for the Synthesis of ALSBA-15 with Large Pore Diameter and High Aluminum Content"*, J. Phys. Chem. B, 108, p.11496-11505.

41) Fulvio, P. F., Pikus, S., Jaroniec, M. (2005). "*Short-time synthesis of SBA-15 using various silica sources*", Journal of Colloid and Interface Science, 287, p.717-720.

42) Colilla, M., Vallet-Regí, M., (2011). *"Ordered Mesoporous Silica Materials",* Comprehensive Biomaterials, 4, p.497–514.

43) Corma, A. (1995). "*Inorganic Solid Acids and Their Use in Acid-Catalyzed Hydrocarbon Reactions*", Chem. Rev., 95, p.559-614.

44) Polyoxometalate, http://en.wikipedia.org/wiki/Polyoxometalate, last accessed date: 01.03.2013.

45) Phosphotungstic acid, http://en.wikipedia.org/wiki/Phosphotungstic_acid, last accessed date: 12.01.2013.

46) Silicotungstic acid http://en.wikipedia.org/wiki/Silicotungstic_acid, last accessed date: 12.01.2013.

47) Phosphomolybdic acid, http://en.wikipedia.org/wiki/Phosphomolybdic_acid, last accessed date: 12.01.2013.

48) Nippon Inorganic Colour & Chemical Co., Ltd. http://www.muki.co.jp/english/product/hpa/index.html last accessed date: 12.01.2013.

49) Kozhevnikov, I.V., (2009). *"Heterogeneous acid catalysis by heteropoly acids: Approaches to catalyst deactivation",* Journal of Molecular Catalysis A: Chemical, 305, p.104–111.

50) Kozhevnikov, I.V., (2007). *"Sustainable heterogeneous acid catalysis by heteropoly acids"*, Journal of Molecular Catalysis A: Chemical, 262, p.86–92.

51) Timofeeva, M.N., (2003). *"Acid catalysis by heteropoly acids",* Applied Catalysis A: General, 256, p.19–35.

52) Soled, S., Miseo, S., McVicker, G., Gates, W.E., Gutierrez, A., Paes J., (1997). *"Preparation of Bulk and Supported Heteropolyacid Salts",* Catalysis Today, 36, Issue 4, p.441–450.

76

53) Corma, A., (1997). *"Solid acid catalysts",* Current Opinion in Solid State and Materials Science, 2, Issue 1, p.63–75.

54) Devassy, B.M., Lefebvre, F., Halligudi, S.B., (2005). *"Zirconia-supported 12-tungstophosphoric acid as a solid catalyst for the synthesis of linear alkyl benzenes",* Journal of Catalysis, 231, p.1-10.

55) Obalı, Z., Sezgi, N.A., Doğu, T., (2011). *"The synthesis and characterization of aluminum loaded SBA-type materials as catalyst for polypropylene degradation reaction",* Chemical Engineering Journal, 176–177, p.202– 210.

56) Aydemir, B., Sezgi, N.A., Doğu, T., (2012). "*Synthesis of TPA Impregnated SBA-15 Catalysts and Their Performance in Polyethylene Degradation Reaction",* AIChE Journal, 58, p.2466-2472.

57) Walendziewski, J. (2002). *"Engine fuel derived from waste plastics by thermal treatment"*, Fuel, 81, p.473-481.

58) Xie, C., Liu, F., Yu, S., Xie, F., Li, L., Zhang, S., Yang, J., (2008). "*Catalytic cracking of polypropylene into liquid hydrocarbons over Zr and Mo modified MCM-41 mesoporous molecular sieve",* Catalysis Communications, 10, p.79–82.

59) Achilias, D.S., Roupakias, C., Megalokonomosa, P., Lappas, A.A., Antonakou, E.V., (2007). "*Chemical recycling of plastic wastes made from polyethylene (LDPE and HDPE) and polypropylene (PP)",* Journal of Hazardous Materials, 149, p.536–542.

60) Donaj, P.J., Kaminsky, W., Buzeto, F., Yang, W., (2012). *"Pyrolysis of polyolefins for increasing the yield of monomers' recovery",* Waste Management, 32, p.840-846.

61) Kaminsky, W., Zorriqueta I.N., (2007). *"Catalytical and thermal pyrolysis of polyolefins"*, J. Anal. Appl. Pyrolysis, 79, p.368-374.

62) Chaianansutcharit, S., Katsutath, R., Chaisuwan, A., Bhaskar, T., Nigo, A., Muto, A., Sakata, Y. (2007). "*Catalytic degradation of polyolefins over hexagonal mesoporous silica: Effect of aluminum addition*", J. Anal. Appl. Pyrolysis, 80, p.360-368.

63) Peterson, J.D., Vyazovkin, S., Wight, C.A., (2001). *"Kinetics of thermal and thermo-oxidative degradation of polystyrene, polyethylene and poly(propylene)"*, Macromol.Chem.Phys., 202, p.775-584.

64) Takuma, K., Uemichi, Y., Sugioka, M., Ayame, A., (2001). *"Production of aromatic hydrocarbons by catalytic degradation of polyolefins over H-Galloslicate"*, Ind.Eng.Chem.Res., 40, p.1076-1082.

65) Sakata, Y., Uddin, M.A., Muto, A., (1999). *"Degradation of polyethylene and polypropylene into fuel oil by using solid acid and non-acid catalysts"*, J.Anal.Appl.Pyrolysis, 51, p.135-155.

66) Uemichi, Y., Makino, Y., Kanazuka, T., (1989). "Degradation of polypropylene to aromatic hydrocarbons over Pt- and Fe-containing activated carbon catalysts", J.Anal.Appl.Pyrolysis, 16, p.229-238.

67) Kumar, G. S., Vishnuvarthan, M., Palanichamy, M., Murugesan, V. (2006). *"SBA-15 supported HPW: Effective catalytic performance in the alkylation of phenol"*, Journal of Molecular Catalysis A: Chemical, 260, p.49-55.

68) Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierrotti, R.A., Jouquerol, J., Siemieniewska, T. (1985). *"Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity"*, Pure and Appl. Chem., 57, p.603-619.

69) Staiti, P., Freni, S., Hocevar, S., (1999). "*Synthesis and characterization of proton-conducting materials containing dodecatungstophosphoric and dodecatungstosilic acid supported on silica*", Journal of Power Sources, 79, p.250-255.

70) *Vazquez, P*., Pizzio, L., Caceres, C., Blanco, M., Thomas, H., Alesso, E., Finkielsztein, L., Lantano, B., Moltrasio, G. and Aguirre, J. (2000). "*Silica-supported heteropolyacids as catalysts in alcohol dehydration reactions"*, Molecular Catalysis A: Chemical, 161, p.223-232.

71) Holmes, S. M., Zholobenko V. L., Thursfield, A., Plaisted, R. J., Cundy, C. S., Dwyer, J. (1998). *"In situ FTIR study of the formation of MCM-41"*, J. Chem. Soc., 94, p.2025-2032.

72) Brodie-Linder, N., Dosseh, G., Alba-Simonesco, C., Audonnet, F., Impéror-Clerc, M, (2008). "*SBA-15 synthesis: Are there lasting effects of temperature change within the first 10 min of TEOS polymerization?"*, Materials Chemistry and Physics, 108, p.73-81.

73) Liu, Q., Wu, W., Wang, J., Ren, X., Wang, Y. (2004). "*Characterization of 12-tungstophosphoric acid impregnated on mesoporous silica SBA-15 and its catalytic performance in isopropylation of naphthalene with isopropanol",* Microporous and Mesoporous Materials, 76, p.51-60.

74) Obalı, Z., Sezgi, N.A., Doğu, T., (2011). "*The synthesis and characterization of aluminum loaded SBA-type materials as catalyst for polypropylene degradation reaction",* Chemical Engineering Journal, 176-177, p.202-210.

75) Coats, A.W., Redfern, J.P. (1964). *"Kinetic parameters from thermogravimetric data"*, Nature, 201, p.68-69.

APPENDIX A

CALCULATION OF TUNGSTOPHOSPHORIC ACID AMOUNT TO BE ADDED TO THE SBA-15 MATERIAL

TPA amount to be added to the solution was calculated according to the following procedure. First of all, silica source was TEOS ($SiC_8H_{20}O_4$) and the weight of TEOS that was used in the experiment was 8.0 g. The molecular weight of TEOS is 208.33 g/mol. Number of moles of TEOS was found using the equation A.1;

$$n_{TEOS} = \frac{M_{TEOS}}{MW_{TEOS}}$$ (A.1)

Number of moles of Si is equal to the number of moles of TEOS (equation A.2).

$$n_{Si} = n_{TEOS}$$ (A.2)

Ratio of tungsten to silica was calculated using equation A.3;

$$Ratio = \frac{n_W}{n_{Si}}$$ (A.3)

where n_W is the mole number of W.

When the mole number of tungsten was calculated, knowing that in 1 mole of TPA ($H_3PW_{12}O_{40}$), there is 12 moles of tungsten; number of moles of TPA is 1/12 of n_W. Therefore, the amount of TPA to be used was found using equation A.4;

$$M_{TPA} = (n_W \ / \ 12) \times MW_{TPA} \qquad (A.4)$$

where M_{TPA} is mass of TPA and MW_{TPA} is the molecular weight of TPA, which is 2880 g/mol. Amount of TPA used in the experiments are given in Table A.1.

Table A.1 Amount of TPA loaded to the SBA-15 materials

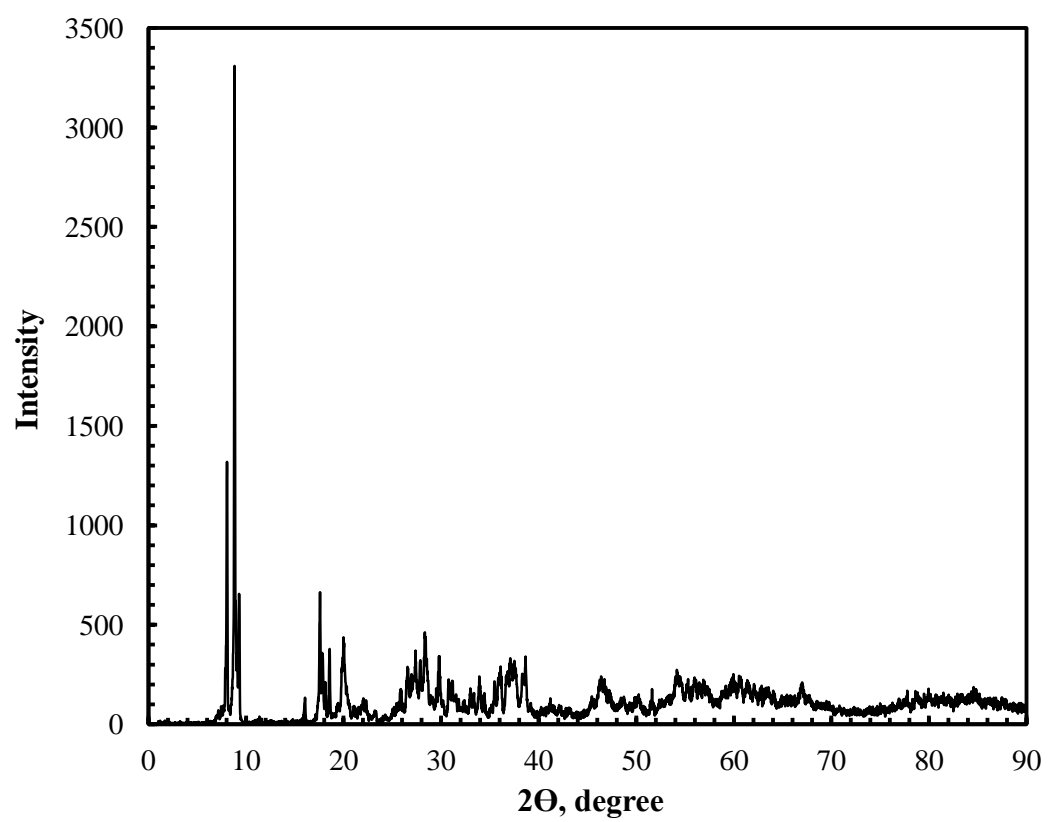| Sample	Amount of TPA loaded (g)
SBA15-TPA0.05	0.46
SBA15-TPA0.10	0.92
SBA15-TPA0.15	1.38
SBA15-TPA0.20	1.84

X-RAY DIFFRACTION PATTERN OF PURE TPA

Figure B.1 X-Ray Diffraction pattern of Pure TPA

APPENDIX C

DETERMINATION OF KINETIC PARAMETERS FROM TGA DATA

In order to determine kinetic parameters from TGA data of the degradation reaction with and without the synthesized catalysts, a similar method in the literature was applied [75]. The model applied to define the kinetics of the reaction is given below,

$$\frac{d\alpha}{dt} = Ae^{-\frac{E}{RT}}(1 - \alpha^n) \qquad (C.1)$$

where A is pre-exponential factor and E is activation energy of the reaction. α is the fraction of polymer decomposed at time t and defined as follows,

$$\alpha = \frac{w_0 - w_t}{w_0 - w_\infty} \qquad (C.2)$$

where, w_o is the initial weight of the sample, w_t is weight at time t, and w_∞ is weight at infinity. Assuming a linear heating rate;

$$a = \frac{dT}{dt} \qquad (C.3)$$

By inserting equation (C.3) into equation (C.1), and after rearranging and integrating, it becomes;

$$\frac{1-(1-\alpha)^{(1-n)}}{(1-n)T} = \frac{AR}{aE}(1 - \frac{2RT}{E})exp(\frac{-E}{RT}) \qquad (C.4)$$

For simplification, assuming that 2RT/E <<1 and taking the natural logarithm of both sides, the following relation is obtained.

$$ln\frac{1-(1-\alpha)^{(1-n)}}{(1-n)T^2} = ln\frac{AR}{aE} - \frac{E}{RT} \qquad (C.5)$$

Equation (C.6) can be applied for first-order reaction where n=1, as well:

$$ln\frac{-ln(1-\alpha)}{T^2} = ln\frac{AR}{aE} - \frac{E}{RT} \qquad (C.6)$$

By using TGA data, values can be inserted into equation (C.5) and (C.6), and after plotting the term on the left-hand side of equations (C.5) and (C.6) as a function of 1/T (Figure C.1 and Figure C.2), activation energy and pre-exponential factor can be obtained from slope and intercept of the straight line. The highest correlation coefficient is the determining factor in deciding the order of the reaction. Therefore, since R^2 value is around 0.96 and greater than the one obtained for a second order assumption, the order of the reaction is accepted as 1.
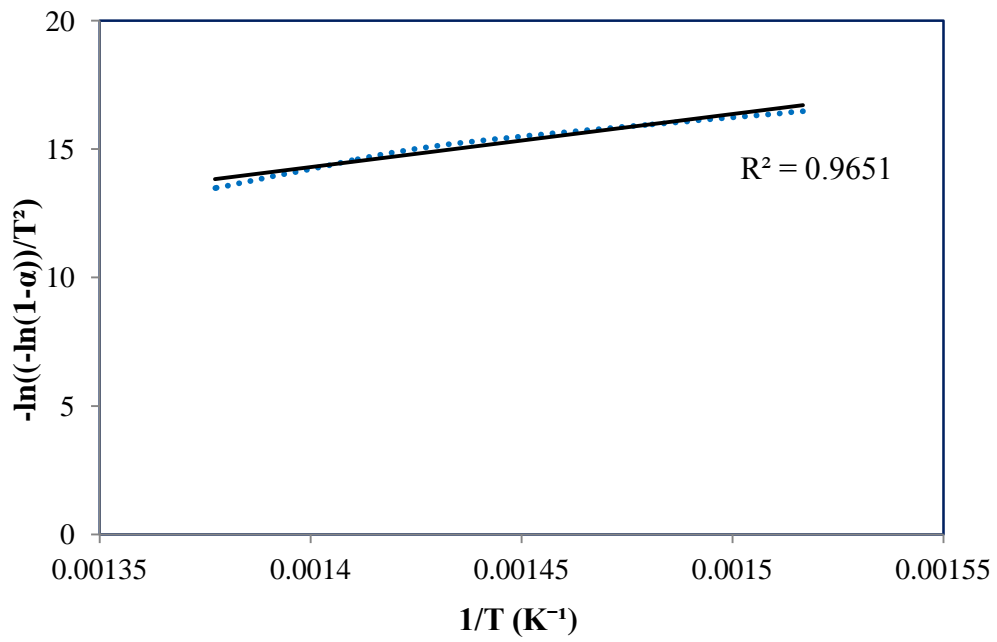
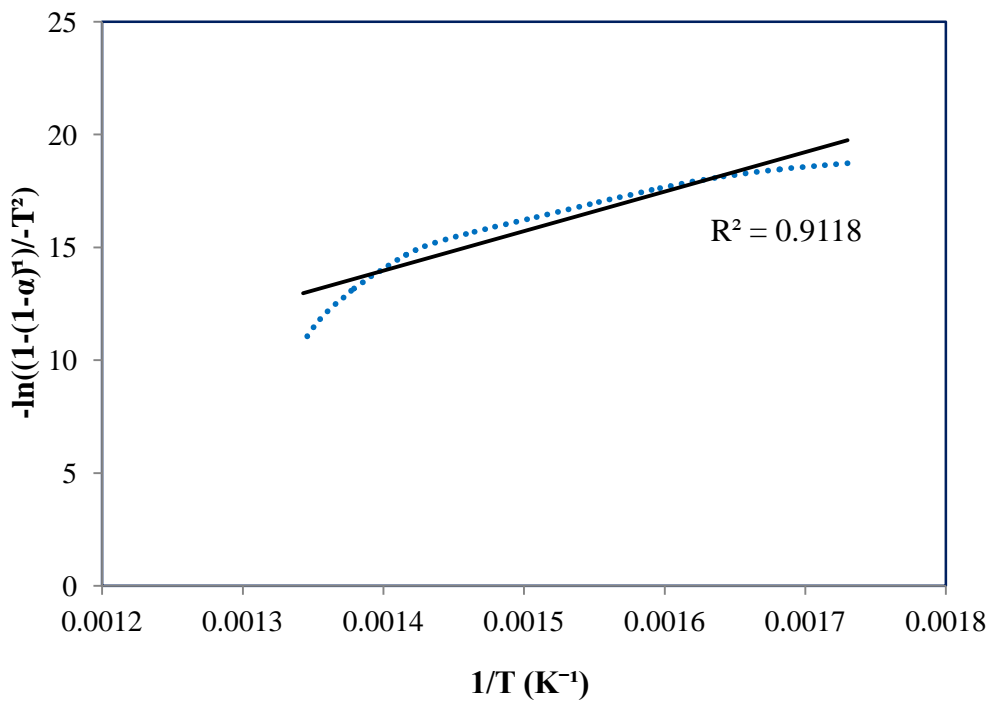**Figure C.1** Determination of the degradation reaction order for n=1

Figure C.2 Determination of the degradation reaction order for n=2